of the claimed invention. Specifically, it is stated in the Office Action that "[s]upport for the limitations of 'values of greater than 24 to 28% aluminum' in claim 8, 'under deposition conditions to . . .', values of greater than 24 to 28% aluminum and 8 to less than 18 wt. % platinum, average nickel concentrations, 'so as to be non-stoichiometric . . .,' and 'oxidizing the aluminide layer . . .' in claim 29, values of greater than 24 to 28% aluminum and values of 8 to less than 18 wt% platinum in claim 56, and values of greater than 24 to 28% aluminum and values of 8 to less than 18 wt% platinum and the claimed average nickel concentrations in claim 89 is totally lacking in the application as originally filed." Office Action at p. 2. As an initial matter, claim 47 was amended in Applicant's Amendment dated April 3, 2002 to include the limitations of now-canceled claim 29, and claim 73 was amended to include the limitations of now-canceled claim 56. Applicant will address the above-enumerated claim rejections for claims 29 and 56 in the context of claims 47 and 73.

Applicant respectfully submits that support for each of these claim limitations was present in the application as originally filed, as is detailed below.

Claims 8 to 10, 12 and 13

Claims 8 to 10, 12 and 13 were rejected under 35 U.S.C. § 112, first paragraph because allegedly "[s]upport for the limitations of 'values of greater than 24 to 28% aluminum' in claim 8 . . . is totally lacking in the application as filed." Office Action at p. 2. Applicant respectfully submits that Fig. 4, along with the accompanying discussion of Fig. 4, discloses that amounts of aluminum greater than 24 weight % up to and including about 28 weight % in the platinum-aluminide region may be used. See, e.g., Fig. 4 (disclosing aluminum weight ranges from 18 to about 31 weight %).

Applicant submits that the rejection of "values of greater than 24 to 28% aluminum" in claim 8 is unsupported. The Examiner rejected this limitation under 35 U.S.C. § 112, first paragraph on the grounds that "the disclosure specifically states that outside the range of . . . 18 to 24% aluminum, the protection afforded is decreased . . . different results are clearly indicated for values . . . greater than 24% aluminum." Office Action at p. 7. The Examiner concludes, with no support, that "hence [the range of 24 to 28% aluminum] is not part of the invention described in the specification giving the desired results." Id.

As an initial matter, Applicant notes that the Examiner agrees that Fig. 4 discloses a range from 18 to 30 wt. % Al. Id. Yet, Applicant submits that the Examiner has impermissibly added an upper limit of 24 wt. % Al to the claims from the specification, which should be withdrawn for a number of reasons. See In re Prater, 415 F.2d 1393, 1404-05 (C.C.P.A. 1969) (limitations of the specifications should not be read into a claim where no express statement of the limitation is included in the claim).

Applicant submits that the Examiner has not met his initial burden of presenting evidence or reasons why persons skilled in the art would not recognize in an applicant's disclosure a description of the invention defined by the claims. See In re Wertheim, 541 F.2d 257, 262, 191 U.S.P.Q. 90, 96 (C.C.P.A. 1976); Ex parte Sorenson, 3 U.S.P.Q.2d 1462, 1463 (B.P.A.I. 1987); MPEP § 2163.04. The reasons given by the Examiner imply that coating performance required to meet some undefined "desired results" of the invention are not met in the rejected range of 24 to 28 wt.% Al. Applicant submits that no support is provided for determining what the Examiner perceives the Applicant's "desired results" to be, and respectfully requests that, if the Examiner

continues to reject this claim for this reason, he provide an objective reference of "desired results" such that the Applicant may meet that basis for rejection.

Second, Applicant submits that the claims of the application, as filed, claim coatings with performance that fall within embodiments that are now covered by the rejected claim limitation of about 24 to 28 wt. % Al. For example, according to claims 1 and 8 as originally filed, the claimed range of about 18 to 24 wt. % Al, in conjunction with the claimed range of about 18 to 45 wt.% Pt, covers any number of coatings that provide performance of less than or equal to 3.5 hours of relative life of the coating measured in hours of exposure per mil of coating when tested in a burner rig in a high-velocity 0.5 ppm salt environment at 2150°F. Application at Fig. 4. Yet, embodiments in the rejected range of about 24 to 28 wt. % Al that likewise show the identical expected life of less than or equal to 3.5 hours have now been rejected as allegedly not capable of achieving the "desired results." Specifically, embodiments having about 8 to about 30 wt.% Pt and 24 to 28 wt.% Al indicate the same performance *or even better performance* of relative life as embodiments having about 18 wt.% Pt and about 20 to 24 wt.% Al. A coating having 26 to 28 wt.% Al and from about 8 to about 16 wt.% Pt actually shows a relative life of greater than or equal to 4.0 hours which is an improvement over those embodiments covered by the initially drafted claims with an upper relative life of about 3.5 hours. Yet, the Examiner has determined that these embodiments having identical or *better* performance *do not* display "desired results." This conclusion is not supportable.

Applicant did not represent in the application that 24 wt.% Al was a critical upper limitation on Al concentration that must be included in the claims. Applicant respectfully submits that the application as filed shows that an embodiment having a relative life of as low as

less than or equal to 3.5 hours fell within the scope of the claims of the invention, and that information would be conveyed to a person of ordinary skill in the art based on the original specification including the claims and also Fig. 4. Applicant therefore requests that this rejection be withdrawn for all of claims 8 to 10, 12 and 13 in its entirety.

Claim 47

Claim 47 is a method claim for forming a thermal barrier coating on a substrate, and the first step thereof reads, "chemical vapor depositing a diffusion aluminide layer on the substrate which includes a nickel base superalloy substrate under deposition conditions effective to provide an outer aluminide layer region comprising a solid solution intermediate phase and an inner diffusion zone region proximate the substrate ..." Applicant submits that the limitation of an outer aluminide layer region with a solid solution intermediate phase and an inner diffusion zone region proximate the substrate is supported in the application as filed as follows. The substrate comprises a nickel base superalloy bulk composition, with a surface region at the substrate surface. Application at p. 3, lines 3 to 5. The surface region is that portion of the coating made according to the invention by the deposition and diffusion of platinum and aluminum which preferably has an integrated aluminum content of at least 18 wt. %. Application at p. 5, lines 6 to 14 and lines 16 to 22; p. 8, lines 18 to 21. The surface region, also referred to as the platinum-aluminide region, is depicted in Figs. 2A and 2B as elements 34, 36 which has been deposited on the surface 31 of the substrate 32. See Application at p. 5 at lines 7 to 11.

The application further discloses that "the chemical compositions of the platinum-aluminide region 34, 36 and *the portion of the substrate 32 immediately adjacent to the*

platinum-aluminide region 34, 36 vary as a function of depth below the surface." See Application at p. 7, lines 27 to 30 (emphasis added). Thus, there is a region comprising *both* a platinum-aluminide region 34, 36 (the surface region) *and* the portion of the substrate 32 immediately adjacent to the platinum-aluminide region 34, 36 that have chemical compositions that vary as a function of depth below the surface, with the platinum-aluminide region 34, 36 (or surface region) defined as that portion having at least about 18 wt. % Al concentration. Application at p. 8, lines 18 to 21. Conversely, this description denotes that there is a portion of the substrate where the chemical composition *does not* vary as a function of depth below the surface as supported by the disclosure that "[t]he remainder of the composition . . . is formed of components of the bulk composition of the substrate alloy, *which is high at a large depth below the surface* 31 *and decreases to a lower value immediately adjacent to the* surface 31." See Application at p. 8, lines 1-4 (emphasis added).

As can be seen from these passages, Applicant disclosed that there is a region of varying chemical composition that varies as a function of depth below the surface which includes both a platinum-aluminide region 34, 36 and a portion of the substrate 32 that is located *immediately adjacent to* the platinum-aluminide region. In addition, Applicant disclosed that there is a portion of the substrate where the bulk substrate composition is high at a large depth below the surface 31 and does not vary as a function of depth below the surface.

Thus, Applicant disclosed in the application as filed that the coating according to the invention includes: (1) a platinum-aluminide region 34, 36 which corresponds to the "solid solution intermediate phase" of claim 47; (2) a portion of the substrate 32 immediately adjacent to the platinum-aluminum region 34, 36 where chemical composition varies as a function of

depth below the surface which corresponds to the "inner diffusion zone region proximate the substrate" of claim 47; and (3) a portion of the substrate 32 where the bulk substrate composition is high and does not vary as a function of the depth below the surface, which corresponds to the "substrate" of claim 47. Together, the platinum-aluminide region 34, 36 and the portion of the substrate 32 in which the chemical composition varies as a function of depth below the surface 31 comprise the "outer aluminide layer region" of claim 47.

There is no requirement that the subject matter of claim 47 be described literally in order to satisfy the written description requirement. See MPEP § 2163.02. Rather, this disclosure satisfies 35 U.S.C. § 112, first paragraph because it reasonably conveys to those skilled in the art that Applicant had possession of the subject matter of this claim limitation at the time of the filing of the application, namely an article including a nickel base superalloy and having a platinum-aluminide coating that comprises (1) the platinum-aluminide region;.(2) the diffusion zone proximate the substrate surface; and (3) that portion of the substrate where the bulk substrate composition is high and does not vary as a function of depth below the surface. A ceramic layer may be added to create a thermal barrier coating system.

Based on this support, Applicant respectfully requests that the rejection under 35 U.S.C. § 112, first paragraph for the limitation of claim 47 "under deposition conditions effective to provide an outer aluminide layer region comprising a solid solution intermediate phase and an inner diffusion zone region proximate the substrate" be withdrawn.

It is stated in the Office Action that claim 47 sets forth "values of 24 to 28% aluminum and values of 8 to less than 18 wt. % platinum" which allegedly are not supported in the original application as filed. Applicant respectfully submits that Fig. 4, along with the accompanying

discussion of Fig. 4, discloses that amounts of aluminum from about 24 to about 28 wt.% and

platinum less than 18 weight % in the platinum-aluminide region may be used. *See, e.g.,* Fig. 4

(disclosing aluminum weight ranges from about 18 to about 31% and platinum weight ranges

from 0 to about 45 weight %).

For the same reasons given above in the discussion of the same rejection for claim 8,

Applicant submits that the claimed range of about 24 to about 28 wt.% Al is supported in the

application as filed based on at least the reason that any number of embodiments that fall within

this range, according to Fig 4, display equivalent or *even better* performance in relative life than

embodiments included in the weight range of Al claimed as originally filed. Therefore the

application as filed conveyed to one of ordinary skill in the art that coating compositions having

24 to 28 wt.% Al provides greater than or equal to 3.5 hours of relative life would be included

within the invention.

Applicant submits that the rejection of "values of 8 to less than 18 wt. % platinum" in

claim 47 is likewise unsupported as is the rejection for values of about 24 to about 28 wt.% Al.

The Examiner likewise rejected this limitation under 35 U.S.C. § 112, first paragraph on the

grounds that "[w]hen viewing values of platinum at less than 18 percent in consideration of the

aluminum value of 18 to 28 %, the coating performance has no life or very poor life. It is clear

from figure 4 that applicants did not have possession of platinum values of 8-18% . . . to achieve

their desired results." Office Action at p. 7. Applicant notes that the Examiner agrees that Fig. 4

discloses a range from 0 to 45 wt. % Pt. Id. Yet, Applicant submits that the Examiner has

impermissibly added a lower limit of 18 wt. % Pt to the claims from the specification, which

should be withdrawn for a number of reasons. See In re Prater, 415 F.2d 1393, 1404-05

(C.C.P.A. 1969) (limitations of the specifications should not be read into a claim where no express statement of the limitation is included in the claim).

Applicant submits that the Examiner has not met his initial burden of presenting evidence or reasons why persons skilled in the art would not recognize in an applicant's disclosure a description of the invention defined by the claims. See In re Wertheim, 541 F.2d 257, 262, 191 U.S.P.Q. 90, 96 (C.C.P.A. 1976); Ex parte Sorenson, 3 U.S.P.Q.2d 1462, 1463 (B.P.A.I. 1987); MPEP § 2163.04. The reasons given by the Examiner imply coating performance required to meet some undefined "desired results" are not met in the rejected range of 8 to 18 wt.% Pt, given the range of 18 to 28 wt. % Al. Applicant submits that no support is provided for determining what the Examiner perceives the Applicant's "desired results" to be, and respectfully requests that, if the Examiner continues to reject this claim for this reason, he provide an objective reference of "desired results" such that the Applicant may meet that basis for rejection.

Second, Applicant submits that the claims of the application, as filed, claim coatings with performance that fall within embodiments that are now covered by the rejected claim limitation of about 8 to 18 wt. % Pt. For example, according to claims 1 and 8 as originally filed, the claimed range of about 18 to 24 wt. % Al, in conjunction with the claimed range of about 18 to 45 wt.% Pt, covers any number of coatings that provide performance of less than or equal to 3.5 hours of relative life of the coating measured in hours of exposure per mil of coating when tested in a burner rig in a high-velocity 0.5 ppm salt environment at 2150°F. See Application at Fig. 4. Yet, other embodiments in the rejected range of about 8 to 18 wt. % Pt that likewise show an expected life of less than or equal to 3.5 hours have now been rejected as allegedly not capable of achieving the "desired results." Specifically, embodiments having about 8 wt.% Pt and 24 wt.

% Al indicate the same performance as embodiments having about 18 wt.% Pt and about 20 to

26 wt.% Al. Yet, the Examiner has determined that certain embodiments having this identical

performance display "desired results," and yet others have not.

Applicant did not represent in the application that 18 wt.% Pt was a critical lower

limitation that must be included in the claims. Applicant respectfully requests that the

application as filed shows that an embodiment having a relative life of less than or equal to 3.5

hours fell within the scope of the claims of the invention, and that information would be

conveyed to a person of ordinary skill in the art based on the original specification including the

claims and also Fig. 4. Applicant therefore requests that this rejection be withdrawn in its

entirety.

Applicant submits that the original application as filed supports the limitation of claim 47

of the platinum-aluminide region (intermediate phase) having "an average nickel concentration

of about 50 to about 60 % by weight." The original application indicated that the platinum-

aluminide region comprises aluminum and platinum which contents "are very high adjacent to

the surface 31, and decrease into the platinum-aluminide region and into the substrate 32."

Application at p. 7, line 30 to p. 8, line 1. Further, substrate components make up the remainder

of this platinum-aluminide region, which according to the disclosure are primarily nickel, cobalt,

and chromium. _See_ Application, page 3, lines 8-9, 25-26; page 8, line 30- page 9, line 1; claims.

As is well known by persons skilled in the art of aluminide and platinum-aluminide

coatings on nickel-base superalloys, one of the two primary mechanisms involved in the

formation of a diffusion coating is outward substrate element diffusion, primarily nickel

diffusion. See G. W. Goward, D.H. Boone, and C.S. Giggins, Formation and Degradation

Mechanisms of Aluminide Coatings on Nickel-Base Superalloys, Transactions of the ASM, Vol. 60, 1967, at p. 237; see also G.W. Goward, Current Research on the Surface Protection of Superalloys for Gas Turbine Engines, 38 Journal of Metals, October 1970, at p. 37. Copies of these references are attached for the Examiner's reference. The authors noted that, "the other major alloying elements [other than nickel] are virtually stationary and are involved only secondarily in the diffusion processes." Id. at p. 238. The diffusion aluminide coatings that were studied were pack cementation aluminide coated on Mar-M200, and comprised 66 wt. % Ni, 14 wt. Al, 7.1 wt. % Co; 1.3 wt. % W; 5.7 wt. % Cr; and 1.4 wt. % Ti. Id. Mar-M200 is a nickel-base superalloy having about 60 wt. % Ni, 10 % Co, 9 % Cr, 12.5 % W, 5 % Al, and 2 % Ti. Id. at p. 228. Thus, it is known to those skilled in the art that aluminide diffusion coatings include Ni concentrations at a higher level than the relative Ni concentration in the alloy substrate due to the preferential outward migration of Ni as compared to the other alloy components to form the remainder of the composition of the diffusion coating. Thus, Ni will make up a greater weight percentage of the remainder of the composition of the platinum-aluminide region than its presence in the bulk substrate alloy. Its weight percentage as a portion of the remainder of the platinum-aluminide region will necessarily be *higher* than its weight percentage in the bulk substrate alloy.

Here, Ni is present in the expressly disclosed nickel-base superalloy substrates at 48 wt. % (RN6); 63 wt. % (RN5); and 69 wt. % (superalloy composition disclosed in original claims 7 and 13). In addition, Applicant expressly noted that the coating of the invention could be used on other nickel-base alloy substrates which have other compositions. Application at p. 6, lines 23 to 25.

As noted, the components of RN6, or RN5, the third exemplary alloy, or any other nickel-base superalloy make up the remainder of the platinum-aluminide region. In claim 47, total wt. % of Pt plus Al ranges from about 26 % to about 73 wt. %, leaving the components of the bulk substrate composition to make up the additional about 27 wt. % to 74 wt. %. Even if Ni migrated into the platinum-aluminide region to make up the remainder of the composition at *only* the same rate as the other alloy components, Ni would constitute up to 36 wt. % on RN6 substrate (74% of 48%); to 47 wt.% on RN 5 substrate (74% of 63%); to 51 wt. % of the platinum-aluminide region composition on the substrate of claims 7(c) and 13(c) (74% of 69%). However, Ni *preferentially* migrates out of the alloy substrate into the diffusion layer at *higher* rates than the other alloy substrate components. Therefore, one skilled in the art of aluminide, and platinum aluminide, diffusion coatings would know that the Ni concentration in the diffusion coating can *exceed* 36 wt. % on RN6 substrate; 47 wt.% on RN 5 substrate; and 51 wt. % of the platinum-aluminide region composition on the substrate of claims 7(c) and 13(c). For other nickel-base superalloys, such as TMS-63 having 72 wt. % nickel, the Ni concentration in the platinum-aluminide region will exceed 53 wt. % (74% of 72%).

Here, Applicant claimed that Ni is present in the platinum aluminide region at about 50 to about 60 wt. %. Given the expressly disclosed substrates and the disclosures of the prior art, Applicant's claim is fully supported factually, and Applicant respectfully requests that the rejection under 35 U.S.C. § 112, first paragraph for failure to provide support for the claimed Ni wt. concentration of about 50 to about 60 wt. % be withdrawn.

It is also stated in the Office Action that the limitation "so as to be non-stoichiometric . . ." is not supported in the original application as filed. However, once the range of Ni

concentration in the platinum-aluminide region is established, it is a matter of calculations to ascertain that the aluminum and nickel, or aluminum and platinum compounds are nonstoichiometric in the substantially beta NiAl phase platinum-aluminide region, or intermediate phase.

The application as filed specifies that the complex formed in the platinum-aluminum region is a single phase, substantially the β NiAl phase of the nickel-aluminum compound. *See* Application, page 8, lines 18-21; page 9, lines 3-4. In such a phase, Ni and Al are, *by definition*, present 50%/50% on an atomic basis. An equiatomic structure of Ni and Al *necessarily* contains 31.5 weight % Al as can be shown by calculation: atomic weight of Ni = 58.69; atomic weight of Al = 26.98; atomic weight of NiAl = 85.67, with 68.5 wt.% Ni and 31.5 wt.% Al. The claimed Al levels as set forth in claim 47 are 18 to 26 weight %, or less than 31.2 weight % Al, which necessarily means that there is insufficient Al in the platinum-aluminide region to form equiatomic NiAl. Thus, Al is nonstoichiometric in the platinum-aluminide region in a NiAl crystal structure.

This Al nonstoichiometry is also necessarily present in a platinum-aluminide region that includes both NiAl and PtAl. When Pt is added to a NiAl compound, the Pt atoms replace Ni one-for-one in the crystal structure. For the maximum claimed Al level of 28 weight % in the platinum-aluminide region of claim 47, with the Ni content maintained between 50 to 60 weight %, the Pt must necessarily range from 12 to no more than 22 weight %. On an atomic basis, resulting Al levels would then necessarily range from 48.9 to 51.8 atomic %, or levels that are nonstoichiometric (either greater than or less than 50 atomic %).

Thus, Applicant respectfully submits that the limitation that the intermediate phase of Al,

Pt, and Ni is nonstoichiometric relative to intermetallic compounds of aluminum and nickel, or

aluminum and platinum, is supported in the application as filed.

Finally, it is stated in the Office Action that the limitation in claim 47 of "oxidizing the

aluminide layer . . ." is totally lacking support in the application as filed. Oxidation of the

surface of a platinum-aluminide layer to provide a protective aluminum oxide scale prior to

addition of a ceramic layer in a thermal barrier coating system is well known in the art, as is

disclosed at page 2, lines 14-15 of the application. The formation of an alumina layer prior to

depositing a ceramic layer has long been known to greatly improve adherence of the ceramic

layer to the bond coat in thermal barrier coating systems. See e.g. Duderstadt et. al., U.S. Patent

No. 5,238,752, col. 2, lines 9 to 13, col. 3, lines 7 to 9, col. 6, lines 45 to 50 and lines 55 to 59;

Nagaraj et. al., U.S. Patent No. 5,427,866, col. 4, lines 20 to 26; Strangman, U.S. Patent No.

4,321,311, col. 3, lines 61-65, col. 4, lines 41 to 47, col. 5, lines 53 to 57; Ulion et. al., U.S.

Patent No. 4,321,310, col. 4, lines 50 to 54; Application at p. 9, lines 13 to 15. Thus, since one

skilled in the art at the time of the filing of the application knows that the Al in the metallic layer

underlying the ceramic layer would preferably be oxidized prior to deposition of the ceramic

layer to improve adherence of the ceramic topcoat, the rejection for lack of written description

should be withdrawn.

Also, an annealing process is disclosed at page 9, lines 6-12 of the application. The

Examiner has explained that "the annealing step on page 9 in no way suggests an oxidation."

Office Action at p. 8. Applicant respectfully submits that annealing processes are well known in

the art as typically performed for protective coatings, as is disclosed in the application. Further,

the annealing procedure typically takes place in a vacuum condition. However, even under the vacuum conditions for typical annealing, sufficient oxygen is available to form an alumina layer from the aluminum on the surface of the protective coating under the temperature and time conditions of 1800°-2000°F for ¼ to 2 hours given in the application. Applicant respectfully submits that one skilled in the art would perform the annealing step under typical vacuum oven conditions in which sufficient oxygen would be present such that alumina would form on the surface.

Further, as explained in the Duderstadt reference, the alumina layer forms during "normal preheating of the coated substrate prior to deposition of the ceramic topcoat." Duderstadt, col. 6, lines 55 to 59. Duderstadt expressly notes that no additional step is required to form the alumina layer because of the fact that alumina forms rapidly upon heating. Id. Further, Strangman discloses that the alumina layer can be formed *after* deposition of the ceramic layer, especially for zirconia based ceramics as are disclosed in the application. Strangman at col. 6, lines 65 to 68.

Here, coupling the knowledge that formation of an alumina layer is desired for ceramic layer adherence; that a typical annealing process in a vacuum environment contains sufficient oxygen to oxidize any aluminum on the surface of the platinum-aluminum region at 1800° to 2000 °F; and that alumina is formed on the surface of the coated substrate during the preheating step of the ceramic deposition, Applicant respectfully submits that the claimed limitation of oxidizing the platinum-aluminide layer to form alumina is disclosed in the application as filed and satisfies the requirements of 35 U.S.C. § 112, first paragraph and that this rejection should be withdrawn.

PATENT
Attorney Docket No. 13DV-13434
21619.000091
Page 20

Claim 73

Although Applicant is unsure whether claim 73 was in fact rejected under § 112, first

paragraph, in good faith Applicant will address the issues raised in regard to claim 56 in the

context of claim 73. Here, claim 56 was rejected for allegedly not providing support in the

application as filed for the limitations of values of greater than 24 to 28 wt.% Al and 8 to less

than 18 wt.% Pt (now found in claim 73 after amendment on April 3, 2002). Applicant has fully

addressed the reasons why these limitations are fully supported in the application as filed with

respect to the arguments above given for claims 8 to 10, 12, and 13 and claim 47, and

respectfully requests that this rejection be withdrawn on at least those same grounds.

Claims 89 to 94

Claim 89 was similarly rejected on the grounds that the limitation of claimed "values of

greater than 24 to 28% aluminum and values of 8 to less than 18 wt. % platinum and the claimed

average nickel concentrations . . . [are] totally lacking in the application as originally filed."

Claim 89 is a method claim for forming a platinum-aluminide surface proximate to the surface of

a nickel-base superalloy substrate, and includes the limitations of "about 18 to about 28% by

weight integrated aluminum content, about 8 to about 45 percent by weight integrated platinum

content and from about 31 percent by weight to about 74 percent by weight integrated nickel

content." As discussed with regard to claim 47, Applicant respectfully submits that Fig. 4, along

with the discussion of Fig. 4, discloses that the rejected weight concentration ranges of aluminum

(24 to 28 wt.%) and platinum (i.e., less than about 18 %) in the diffusion layer may be used. See,

e.g., Fig. 4 (disclosing aluminum weight ranges from about 18 to about 31 % and platinum

weight ranges from 0 to about 45 weight %); see also Application, page 9, line 24, through page

10, line 2 (discussing that the region of significantly improved performance for platinum-aluminum regions has an integrated aluminum content of from about 18 to about 24 percent by weight and an integrated platinum content of from about 18 to about 45 percent by weight, although "[o]utside of these limits, protection afforded by the surface region decreases.")

Further, given the claimed weight concentration ranges of aluminum and platinum, the disclosure of the balance of the nickel concentrations necessarily follows. As discussed with regard to claim 47, the application, as filed, states that the substrate components make up the remainder of the surface region. In addition, as discussed for claim 47, nickel preferentially migrates into the platinum aluminide layer (or surface region) over the other alloy substrate components. See also Application, page 3, lines 8-9, 25-26; page 8, lines 1-4, lines 30-31; claims. The nickel concentration in the platinum aluminide layer can thus range from about 27 weight % to about 74 weight %, based on Al plus Pt weight concentrations totaling about 26 weight % to about 73 weight %, assuming substantially only nickel migrates from the substrate into the aluminide layer.

This range of weight % Ni is further supported by the specific examples of substrates disclosed starting at page 5, line 23 through page 6, line 10, which set forth a range of nickel content of exemplary substrates of about 49 to about 69 % by weight nickel. In claim 89, given the limitations on weight concentrations of aluminum and platinum and the disclosure that the remainder of the diffusion layer is made up of the bulk substrate composition, migrating elements from the bulk substrate composition must necessarily make up from about 31 % by weight to about 74 % by weight of the diffusion layer (as determined by adding together the lower aluminum and platinum weight concentrations and also the higher aluminum and platinum

weight concentrations). As the Ni preferentially migrates over the other components of the substrate, the weight % of Ni in the aluminide layer will rise to the point where only Ni migrates, which is 31 to 74 weight %. The fully disclosed nickel concentration in the platinum aluminide layer in the application is thus about 27 up to about 74 % by weight, and completely supports the limitation in claim 89 of about 31 to about 74 percent by weight Ni.

Thus, Applicant respectfully submits that the application, as filed, supports the disclosure of 24 to 28 wt.% aluminum, as low as zero, and certainly 8 weight % platinum, and about 31 to about 74 weight % nickel in the platinum aluminide region.

For all the reasons set forth above, Applicant respectfully requests the withdrawal of the claim rejections for claims 89-94 under 35 U.S.C. § 112, first paragraph.

IV.   Double Patenting Rejection

Claims 8-13, 16-18, 47, 73 and 89 to 94 have been provisionally rejected under 35 U.S.C. § 101 obviousness-type double patenting as that of claims 8-13, 16-18, 47, 71 and 87-92 of copending Application No. 09/244,578.

Applicant acknowledges this rejection, and will amend or cancel claims 8-13, 16-18, 47, 73 and 89-94 or file a terminal disclaimer pursuant to 37 C.F.R. § 1.321(c) for the later of these two applications to issue if this rejection is appropriate at that time.

V.   Claim Rejections under 35 U.S.C. § 102(e)

Claims 8-13 have been rejected under 35 U.S.C. § 102(e) as allegedly being anticipated by Murphy, U.S. Patent No. 5,716,720 ("Murphy"). The Office Action rejection apparently is based on the premise that col. 3, lines 55-58, col. 4, lines 5-19, col. 5, N5 substrate in the examples, and the claims of Murphy necessarily describe the invention in a patent granted on an

application for patent by another (Murphy) filed in the United States before the invention thereof by Applicant. Office Action at p. 4.

Applicant respectfully submits that the cited reference does not anticipate claims 8-13 as amended. Specifically, independent claim 8, from which claims 9 through 13 depend, has been amended to clarify that Pt diffusion is separate from and performed prior to Al deposition and diffusion, which distinguishes Murphy over the claimed invention.

"A claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art reference," citing Verdegaal Bros. v. Union Oil Co. of California, 814 F.2d 826, 831 (Fed. Cir. 1987).

No mention is made in Murphy of depositing a layer of platinum upon a substrate surface and diffusing platinum from the layer of platinum into the substrate surface, in a step separate from aluminum deposition and diffusion. See Murphy, col. 2, lines 45-51 ("The platinum modified diffusion aluminide layer preferably is formed by depositing a layer of platinum or alloy thereof on the substrate and chemical vapor depositing aluminum on the platinum covered substrate under high temperature and low aluminum activity conditions to form the inner diffusion zone and the outer intermediate phase region.") Also see col. 4, lines 25-28. In fact, the process disclosed in Murphy expressly *does not* diffuse platinum after the platinum is deposited on the substrate surface in a step separate from aluminum deposition and diffusion. *See* Murphy, col. 4, lines 45-48 ("For example, generally, the substrate is electroplated with a 9-11 milligram/centimeter squared platinum layer (e.g. 2 mil thick Pt layer) and then subjected, *without a Pt prediffusion treatment*, to CVD aluminizing . . .") (emphasis added).

Since Murphy does not disclose each and every element as set forth in independent claim 8 as amended, Applicant respectfully submits that Murphy does not anticipate claims 9-13 and requests that this rejection be withdrawn.

VI.   35 U.S.C. § 103 Rejections

Claims 8, 10-13, 16-18, 73, 89-94, and 112 have been rejected as allegedly being obvious pursuant to 35 U.S.C. § 103(a). Applicant respectfully submits that these claims, either as amended or as originally filed, are not obvious over the cited references because the cited references do not show either (1) that the references teach or suggest all the claim limitations in each instance and/or (2) a suggestion or motivation to modify the references or to combine reference teachings.

A.   Claims 16-18 and 89-94 over Murphy

Claims 16-18 and 89-94 have been rejected under § 103(a) as being allegedly unpatentable over Murphy because, although "Murphy does not explicitly disclose the aluminum source activity as recited in claims 16 and 87 [sic] . . . Murphy discloses deposition at low aluminum activity conditions at col. 4, lines 25-30 which one of ordinary [skill in the art] would consider to include values in the claimed range . . . Therefore, use of the claimed aluminum values would have been obvious absent evidence showing criticality of using these values over other 'low' activities." Office Action at page 4. Independent claims 16 and 89 recite, *inter alia,* providing a source of aluminum having an activity of about 40 to about 50 atomic percent as measured in a pure nickel foil, and depositing aluminum onto a substrate by using an aluminum source having the same aluminum activity.

Applicant respectfully submits that Murphy does not render independent claims 16 and 89 as amended obvious because Murphy does not teach or suggest all the claim limitations, specifically the claim limitation of a heating step following platinum deposition on the substrate surface separate from and prior to aluminum deposition onto the platinum layer. The process disclosed in Murphy expressly teaches away from the step of diffusing platinum after platinum is deposited on the substrate surface separately from the aluminum deposition step. *See* Murphy, col. 4, lines 45-48 ("For example, generally, the substrate is electroplated with a 9-11 milligram/centimeter squared platinum layer (e.g. 2 mil thick Pt layer) and then subjected, *without a Pt prediffusion treatment,* to CVD aluminizing . . .") (emphasis added). Thus, since Murphy does not teach or suggest each and all the claim limitations of claims 16 and 89 as amended, this reference does not support a *prima facie* case of obviousness. Further, this argument extends to claims 17-18, dependent from claim 16, and claims 90-94, dependent from claim 89. Applicant thus respectfully requests that this rejection be withdrawn.

B. Claim 16 over Shankar

Claim 16 has been rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over Shankar, U.S. Patent No. 4,501,776 ("Shankar") because, "Shankar discloses the claimed process at col. 1, line 50 to col. 2, line 41, with the exception that the ranges for the process conditions taught by Shankar overlap the claimed ranges."

Applicant respectfully submits that Shankar does not disclose or suggest each and every limitation of claim 16 as amended, and therefore claim 16 is patentable over Shankar. Specifically, claim 16, as amended, contains the limitations of "providing a substrate having a nickel-base superalloy substrate bulk composition," "providing a source of aluminum in contact

with the substrate surface, the source having an activity of about 40 to about 50 atomic percent as measured in a pure nickel foil," and a "substantially single phase platinum-aluminide surface region," which limitations are not disclosed or suggested in Shankar.

Initially, the protective diffusion layer of Shankar is a two phase coating in contrast to the single phase surface region of amended claim 16. See Shankar at col. 2, lines 16-20; Figs. 2, 3. For this reason alone, the invention is not obvious under Shankar.

In Applicant's specification, nickel-base superalloys are repeatedly referred to as a preferred substrate. See, e.g., Application, page 2, lines 27-28; page 3, lines 4-5, 17; page 4, line 1; page 5, line 20 to page 6, line 25; page 9, line 21; claims, Abstract. Shankar, however, discloses a method of forming a protective diffusion layer on nickel, cobalt or iron base alloys. The lack of disclosure of a nickel base superalloy in Shankar is contrasted by Applicant's disclosure that "this improved performance [of the platinum-aluminide coating] is particularly important for these advanced single-crystal nickel base superalloy substrates . . . diffusional effects are accordingly more important." Application at p. 6, lines 11 to 18. The lack of disclosure of process conditions in Shankar is underscored by the fact that Shankar produces a two phase diffusion layer while the platinum-aluminide region of the invention is substantially a single phase. Applicant noted in the disclosure that the processing conditions determine "the amount of aluminum transferred to the substrate and diffused into the substrate" and that "preferred processing produces an activity of between 40 and 50 atomic percent in a pure nickel foil." Application at p. 7, lines 13 to 24. Thus, the lack of disclosure in Shankar of the process conditions of the invention, in conjunction with the different structure of the product of Shankar, shows that any overlapping ranges disclosed in Shankar do not render the invention obvious, in

light of no teaching that changing the processing conditions would result in the substantially single phase claimed invention rather than the two phased layer of Shankar.

Since Shankar does not disclose or suggest each and every claim limitation of claim 16 as amended, Applicant respectfully submits that this reference cannot support a *prima facie* case of obviousness. Such criteria include a showing that the reference teaches or suggests all the claim limitations or a showing of a suggestion in the art that the reference should be modified to include all of Applicant's claimed limitations. For at least these reasons, Applicant respectfully requests this rejection under 35 U.S.C. § 103(a) over Shankar be withdrawn.

C.   Claim 17 over Shankar in view of Duderstadt

Claim 17 has been rejected under 35 U.S.C. § 103(a) as allegedly unpatentable over Shankar in view of Duderstadt *et. al.*, U.S. Patent No. 5,238,752 ("Duderstadt") because, "Shankar lacks teaching of EB vapor depositing a columnar structure yttria stabilized zirconia TBC . . . However, because Duderstadt discloses that deposition of such TBC on platinum aluminide coating by EBPVD provides the advantages described at col. 5, lines 1-10 (abstract, col. 7), it would have been obvious to have deposited the TBC to achieve these advantages." Office Action at page 5.

Applicant submits that claim 17, as amended by claim 16 to include the limitation of a substantially single phase platinum-aluminide surface region, is not rendered obvious over Shankar in view of Duderstadt for at least the reason that neither Shankar nor Duderstadt discloses a substantially single phase platinum-aluminide region. As mentioned previously, Shankar discloses that his diffusion layer has two phases, and Duderstadt does not address the phase of the disclosed platinum-aluminide. However, Duderstadt does present an example of a

platinum aluminide made according to the invention on a Rene N5 substrate, where platinum was electroplated and aluminum was deposited by pack cementation. Duderstadt at col. 10, lines 9 to 15. No processing conditions were provided. The coating was designated as Chromalloy RT 22. A comparison to the cited Conner ASME reference discloses that the Chromalloy RT 22 coating is a two phase coating. See Conner at p. 3. Thus, there is no teaching in Duderstadt that the platinum-aluminide made in that disclosure is substantially a single phase, and such a substantially single phase coating is also not inherent according to the sample provided therein.

In the rejection, no objective basis was established for combining the teachings of the references; instead, a selection of helpful portions from each reference was made while ignoring these unhelpful portions that disclose a two-phase platinum aluminide coating.

Also, neither Shankar nor Duderstadt disclose or suggest the activity limitation of the aluminum source as set forth in amended claim 16, from which claim 17 depends. In fact, neither Shankar nor Duderstadt disclose any limitation on the activity of the aluminum source, and therefore each and every claim limitation of claim 17 would not have been suggested to a person of ordinary skill by even the improper combination of the cited references.

Applicant submits that each and every limitation of claim 17 is not disclosed or suggested in the cited references and withdrawal of this obviousness rejection is requested.

D.   **Claim 18 over Shankar in view of Wukusick**

Claim 18 has been rejected as allegedly unpatentable over Shankar in view of Wukusick et. al., U.S. Patent No. 5,100,484 ("Wukusick"). It was stated in the Office Action that Shankar teaches nickel-based alloy turbine substrates but does not disclose the contents of aluminum and rhenium. However, claim 18 was rejected over the combination of Shankar and Wukusick

"because Wukusick discloses that substrates with the claimed components are known alloys for use as turbine parts, it would have been obvious to use such conventional substrates with the expectation of their being effective for turbine substrates." Office Action at page 5.

Again, Applicant submits that the amendment to claim 16 to add the limitation that the platinum-aluminide coating be substantially single phase overcomes this rejection because the cited references do not disclose each and every limitation of claim 18, and respectfully requests withdrawal of the same.

E. Claims 73 and 112 over Conner in view of Duderstadt

Claims 73 and 112 have been rejected as allegedly unpatentable under 35 U.S.C. § 103(a) over Conner *et. al.*(*Evaluation of Simple Aluminide and Platinum Modified Aluminide Coatings on High Pressure Turbine Blades after Factory Engine Testing - Round II*) in view of Duderstadt because, "Conner discloses the claimed process . . . with the exception that Conner does not teach depositing a TBC . . . Application of a TBC would have been obvious in view of Duderstadt." Office Action at page 6. Applicant submits that claim 73 has been amended to include the limitation that the diffusion aluminide layer is substantially single phase and therefore most of the examples of Conner do not disclose a single phase platinum aluminide coating. Conner does disclose a single example which indicates a single phase as the MDC-150L coating. Conner at p. 3. However, the MDC-150L coating concentration gradient of Pt and Al which is depicted in Fig. 3 shows that the Pt concentration does not decrease with increasing depth into the aluminide layer from a high value adjacent to the surface, as required by claim 73. Instead, the Pt concentration gradient increases for about the first 25 microns of distance from the surface, at which time it begins decreasing with increasing depth. Conner at p.

4, Fig. 3, MDC-150 on SC Alloy. Finally, neither Duderstadt nor Conner discloses the weight % ranges of Pt and Al set forth in claim 73. Claim 73 recites a Pt concentration from about 8 to about 45 wt. %, and Al from about 18 to about 28 wt. %. In contrast, Duderstadt has no disclosure on the composition of the platinum aluminide coating in terms of wt.% Pt or Al, and none of the examples in Conner disclose Pt concentration up to 45 wt. %.

Thus, neither of the Conner or Duderstadt disclosures discloses each and every limitation of claim 73 or claim 112. For at least these reasons, Applicant submits that claims 73 and 112 are not obvious over Conner in view of Duderstadt and that the § 103 obviousness combination rejection should be withdrawn.

F.   **Claims 8, 10, 11, and 89-92 over Conner in view of Shankar**

Claims 8, 10, 11, and 89-92 have been rejected under 35 U.S.C. § 103(a) as allegedly unpatentable over Conner in view of Shankar. Claim 8 has been amended to include the limitation that the platinum-aluminide surface region is substantially a single phase. Claim 89 as filed included the limitation that platinum-aluminide surface region was substantially single phase. As argued previously, Shankar does not disclose a substantially single phase diffusion layer. Conner discloses only one example that may include a substantially single phase surface region, the MDC-150L coating. However, claims 8 and 89 include the further limitations that the Pt concentration is from about 8 to about 45 wt. %. Neither Conner nor Shankar discloses a Pt concentration gradient of about 8 to about 45 wt. Further, neither Conner nor Shankar discloses or suggests the annealing limitation of claims 10 and 92.

Applicant submits that claims 8 and 89, and dependent claims 10, 11, 90, 91 and 92 therefrom, are not obvious over Conner in view of Shankar for at least the reason that these

references do not recite each and every limitation of independent claims 8 and 89. Applicant thus respectfully requests that this rejection be withdrawn.

G. Claims 93 and 94 over Conner in view of Shankar and further in view of Duderstadt

Claims 93 and 94 have been rejected under 35 U.S.C. § 103(a) as allegedly unpatentable over Conner in view of Shankar and further in view of Duderstadt because, "[a]pplication of a TBC would have been obvious in view of Duderstadt for the reasons set forth above." Office Action at p. 6.

For the same reasons given above, Applicant submits that claim 89 is not obvious in view of these references because none of Conner, Shankar or Duderstadt discloses the range of wt. % of Pt, the substantially single phase surface region, or the processing conditions as claimed. Claims 93 and 94 depend from claim 89. Because these references do not disclose each and every limitation of claim 89, they do not disclose each and every limitation of dependent claims 93 or 94. Applicant thus requests that this rejection be withdrawn.

H. Claims 12 and 13 over Conner in view of Shankar and further in view of Wukusick

Claims 12 and 13 have been rejected under 35 U.S.C. § 103(a) as allegedly unpatentable over Conner in view of Shankar and further in view of Wukusick because, "[u]se of the claimed substrates would have been obvious in view of Wukusick for the reasons set forth above." Office Action at page 6.

For the same reasons given by Applicant above regarding amended claim 8, these references do not disclose each and every limitation of claims 12 and 13 because they do not disclose each and every limitation of amended claim 8. Specifically, these references do not

PATENT
Attorney Docket No. 13DV-13434
21619.000091
Page 32

disclose the processing conditions, the range of Pt wt. % concentrations, or that the platinum-aluminide surface region is substantially single phase set forth in amended claim 8. For at least these reasons, Applicant submits that these references do not support a *prima facie* case of obviousness and requests that this obviousness rejection be withdrawn.

VII.   CONCLUSION

Applicant submits that the application is in condition for allowance and respectfully requests entry of this amendment and a notice of allowance for all the pending claims. Should the Examiner determine that any further action is necessary to place this application in condition for allowance, the Examiner is kindly requested and encouraged to telephone Applicant's undersigned representative at the number listed below.

Applicant authorizes the fee of $920.00 for a three month extension of time to be deducted from Deposit Account No. 50-0206.

Date: November 15, 2002

Respectfully submitted,

HUNTON & WILLIAMS,

By: _____
Nancy J. Flint
Registration No. 46,704
1111 Brickell Avenue, Suite 2500
Miami, Florida 33131
Tel. (305) 810-2522
Fax: (305) 810-2460

FAX RECEIVED

NOV 1 8 2002

OFFICIAL   GROUP 1700

APPENDIX A

Marked up Version of Amended Claims

8.   (Twice amended) A method for preparing an article having a platinum-aluminide surface region, comprising the steps of:

> providing a substrate having a nickel-base superalloy substrate bulk composition and a substrate surface;

> depositing a layer of platinum upon the substrate surface, thereafter;

> diffusing a platinum from the layer of platinum into the substrate surface, thereafter;

> providing a source of aluminum; and thereafter

> diffusing aluminum from the source of aluminum into the substrate surface for a time sufficient to produce a substantially single phase surface region at the substrate surface, the surface region having an integrated aluminum content of from about 18 to about 28 percent by weight and an integrated platinum content of from about 18 to about 45 percent by weight, balance components of the substrate bulk composition.

16.   (Twice amended) A method for preparing an article having a platinum-aluminide surface region, comprising the steps of:

> providing a substrate having a nickel-base superalloy substrate bulk composition and a substrate surface, thereafter;

> depositing a layer of platinum about 0.0003 inches thick upon the substrate surface, thereafter;

heating the substrate and layer of platinum to a temperature of about 1800-2000°F for a time of about 2 hours, thereafter;

providing a source of aluminum in contact with the substrate surface, the source of aluminum having an activity of about 40 to about 50 atomic percent as measured in a pure nickel foil; and simultaneously

heating the substrate surface and the source of aluminum to a temperature of about 1925-2050°F for a time of from about 4 to about 16 hours to form a substantially single phase platinum-aluminide surface region.

47.   (Twice amended) A method of forming a thermal barrier coating on a substrate, comprising:

chemical vapor depositing a diffusion aluminide layer on the substrate which includes a nickel base superalloy substrate under deposition conditions effective to provide an outer aluminide layer region comprising a substantially single phase solid solution intermediate phase and an inner diffusion zone region proximate the substrate;

said intermediate phase including an average aluminum concentration in the range of about 18 to about 28 % by weight, an average platinum concentration in the range of about 8 to about 45 % by weight, and an average nickel concentration of about 50 to about 60 % by weight so as to be non-stoichiometric relative to intermetallic compounds of aluminum and nickel, or aluminum and platinum, said outer aluminide layer region being substantially free of phase constituents other than said intermediate phase;

oxidizing the <u>diffusion</u> aluminide layer under temperature and oxygen

partial pressure conditions effective to form an alpha alumina layer; <u>and</u>

depositing a ceramic thermal barrier layer on the alumina layer. [; and]

wherein said intermediate phase further comprises a surface, distant from

said inner diffusion zone region, and the intermediate phase includes the

aluminum content and the platinum content which is relatively high adjacent to

the surface and decreases with increasing depth into the intermediate phase.

73.   (Twice amended) A method of forming a thermal barrier coating on a substrate,

comprising:

chemical vapor depositing a <u>substantially single phase</u> diffusion aluminide

layer on the substrate which includes a nickel base superalloy substrate;

said aluminide layer including an average aluminum concentration in the

range of about 18 to about 28 % by weight and an average platinum concentration

in the range of about 8 to about 45 % by weight, wherein said aluminide layer

further comprises a surface, and includes the aluminum content and the platinum

content which is relatively high adjacent to the surface and decreases with

increasing depth into the aluminide layer and the substrate; and

depositing a ceramic thermal barrier layer on the aluminide layer.

89.   (Amended) A method of forming a platinum-aluminide surface region proximate

to the surface of a nickel-base superalloy substrate, comprising:

forming a platinum layer at the substrate surface by a method selected from the group

consisting of electroplating, sputtering and metallo-organic chemical vapor deposition,

thereafter;

heating the substrate to a temperature of from about 1800 to about 2000°F for a time of

about 2 hours; and thereafter[;]

depositing aluminum onto the nickel-base superalloy substrate by using an aluminum

source and diffusing said aluminum into the substrate surface at an elevated temperature, at an

aluminum activity of from about 40 to about 50 atomic percent in a pure nickel foil, and for a

time of from about 4 to about 16 hours to form a substantially single phase platinum-aluminide

surface region proximate the substrate surface, said platinum-aluminide surface region

comprising from about 18 percent to about 28 percent by weight integrated aluminum content,

from about 8 to about 45 percent by weight integrated platinum content and from about 31

percent by weight to about 74 percent by weight integrated nickel content.

Formation and Degradation Mechanisms of Aluminide Coatings on Nickel-Base Superalloys

G. W. GOWARD, D. H. BOONE and C. S. GIGGINS

ABSTRACT. The formation and degradation mechanisms of an aluminide coating on Mar-M200, a typical high-strength nickel-base superalloy, have been investigated. For the particular coating conditions used (pack cementation with a high aluminum activity), the coating is formed by predominant inward diffusion of aluminum and many of the composition and structural features of the substrate alloy are, therefore, reproduced in the coating. Discrete tungsten and chromium-rich phases are formed in the initial coating layer primarily because of limited solubility of these elements in the aluminum-nickel intermetallic coating matrix phase. Subsequent short-time elevated-temperature heat treatment causes increased counter-diffusion of nickel, resulting in the formation of two additional diffusion layers and further precipitation of refractory alloying element phases. These results are generalized to explain how a variety of coating structures can be formed by predominant inward aluminum diffusion, predominant outward nickel diffusion and all intermediate possibilities depending on the particular coating conditions selected. Oxidative degradation involves loss of aluminum from the coating by repeated formation and spallation of protective aluminum oxide and subsequent formation of more complex, less protective oxides. Degradation rates of various coating systems will vary in accordance with propensity for singular aluminum oxide formation and with the degree of spallation of this or other more complex oxides.

THE ACHIEVEMENT of higher strengths in nickel-base superalloys for gas turbine engine applications has generally been attained only at the expense of oxidation resistance. The basic oxidation resistant Nichrome (80% Ni – 20% Cr) composition has given way to multiphase lower chromium alloys which oxidise more rapidly by a number of complex mechanisms. In the past two decades, aluminide protective coatings have been developed which have allowed these alloys to be used at higher temperatures than possible in the uncoated condition. Appreciably extended lifetimes, in the range of 1600 to 1800 F metal temperatures, have been attained with coatings applied to nickel-base superalloys by relatively simple aluminising techniques.

Although aluminide coated superalloys have been widely used for a number of years, very little is understood about the chemical and metallurgical processes which occur during the formation and degradation of these complex systems. The superior high-temperature oxidation resistance of the intermetallic compound NiAl, upon which superalloy aluminide coatings are based, indicates that further significant improvements in protection should be possible with this class of coatings. To provide a basis for such improvements, detailed studies have been undertaken on the composition, structure, and formation and degradation mechanisms of several model coating-alloy systems. This paper presents results obtained for one such system, specifically, a pack cementation aluminide coating on Mar-M200, a typical high-strength cast-nickel-base superalloy. Although only one coating method, and one substrate, are described in this paper, it has been found that the principles involved are generally common to most, if not all, aluminide coating-superalloy systems. The results presented serve, therefore, as a basis for prediction of the behavior of a variety of related systems.

EXPERIMENTAL PROCEDURES

COATING SYNTHESIS

Coupons of as-cast Mar-M200 (composition 0.15% C, 10% Co, 9% Cr, 12.5% W, 5% Al, 2% Ti, 0.05% Zr, 0.015% B, bal Ni) of suitable size for metallographic, x-ray diffraction and electron-beam microprobe analysis were coated by a typical pack cementation procedure. Coatings were formed by immersing the coupons in a mixture consisting typically of 15% Al (−325 mesh powder), 3% NH₄Cl (activator) and 82% Al₂O₃ (120 mesh, inert filler), and heating in a suitable container in a laboratory furnace fitted

Goward, Boone and Giggins

for argon flushing during the coating formation cycle. Coating thickness is a function of pack composition and time and temperature of the heating cycle. In general these variables were adjusted in this study to yield coatings of thickness suitable for the analytical techniques used to determine structure and composition. These thicknesses (2 to 5 mils) fall within the range normally used for protection of gas turbine engine hardware.

HEAT TREATMENT AND OXIDATION

To study the various composition and structure changes which occur during the lifetime of the coating-alloy system, specimens were subjected to a variety of inert atmosphere and oxidative heat treatments in the range of 2000 to 2200 F. These heat treatments can be divided into two general categories: (a) short term, of the order of a few hours, either in air or inert atmosphere (argon), which cause significant changes in the structure and composition of the coating but do not contribute significantly to its degradation; and (b) long term, of the order of hundreds of hours, in air which cause further structure and composition changes and contribute to degradation of the system. Accelerated oxidation in a high-velocity hot-gas stream was employed in a few cases to speed up the degradation processes. Since thermal cycling accelerates oxidative degradation, all extended oxidation heat treatments used in this work involved some mode of thermal cycling. If oxidation was performed in a laboratory furnace, specimens were cooled to room temperature once every hour. Dynamic testing involved similar times of thermal cycling. For the purpose of this study, no distinction between simple oxidation and accelerated oxidation in a dynamic environment is necessary, since the phase changes occurring within the coating are virtually identical for both processes; only the time scale is different. By the same token, since the oxidative treatments used do not necessarily reflect turbine engine operating conditions, no conclusions should be drawn with respect to the practical lifetime of the particular system studied.

PHASE IDENTIFICATION AND ANALYSIS

Suitable sections of coated specimens were mounted in epoxy resin and ground and polished using standard metallographic techniques. The final polish was on micro-cloth wheels using 0.1 μ alumina in water. Two etchants were used as follows: No. 1, swab etch with a mixture of 30 ml each of lactic and acetic acids, 20 ml of conc hydrochloric acid and 10 ml of conc nitric acid; and No. 2, immersion-etch in a solution composed of one part each of 14% aqueous sodium hydroxide and saturated aqueous potassium permanganate. The first etch defines the general coating structure; the β phase (NiAl) etches while γ' (Ni₃Al) and γ (Ni solid solution) are selective for car-

bides in the coating and base alloy; M₆C stains brown, M₂₃C₆ varies between green and pale blue tints and MC is multicolored. Electron microscopy was used for examination of a few specimens but no significant additional information was obtained with this technique.

Distributions of the major elements (Ni, Al, Co, W, Cr and Ti) in the coatings and substrates were determined with a Cambridge Microscan electron probe microanalyser (hereinafter designated as EPM). The incident electron beam was operated at an acceleration potential of 25 kv and its diameter at the specimen surface was maintained at 2 μ or less. Qualitative analyses of the phases present were obtained from electron backscatter and x-ray images over representative areas of the microstructures. Relative concentrations of the elements are shown by the contrast of light and dark areas in the x-ray images, with light areas corresponding to high concentration. Quantitative analyses of the phases were obtained by slow scanning the beam across the coating-substrate composites. Chart-recorded concentration profiles, exhibiting both peak and background intensities, were obtained from the phases traversed and from elemental standards. First-order approximations of the weight fractions of each element were corrected for matrix fluorescence and absorption effects to yield values accurate to within ±10% of the amount present.

Standard x-ray diffraction (hereinafter designated as XRD) techniques were employed for phase identification in the coatings. Both CuKα and CrKα radiations were found to be suitable for identification of the phases. The surfaces of specimens,

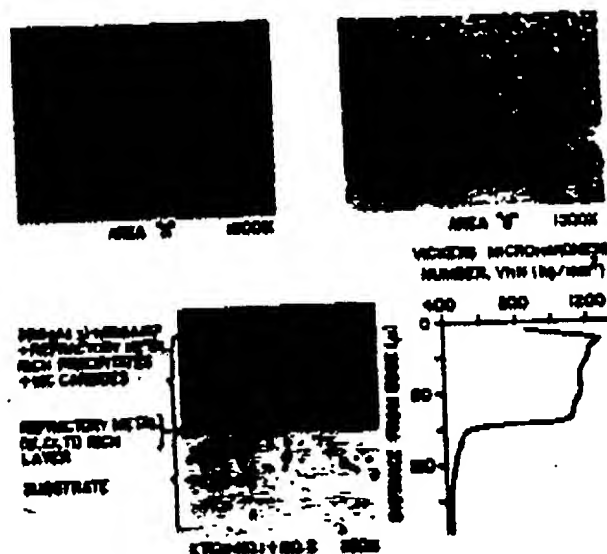Fig. 1. Microstructure, microhardness profile and phase identification for peak aluminized Mar-M200. Asreceived condition: coating cycle 3 hr at 1900 F. Original magnifications reduced 50% in reproduction.
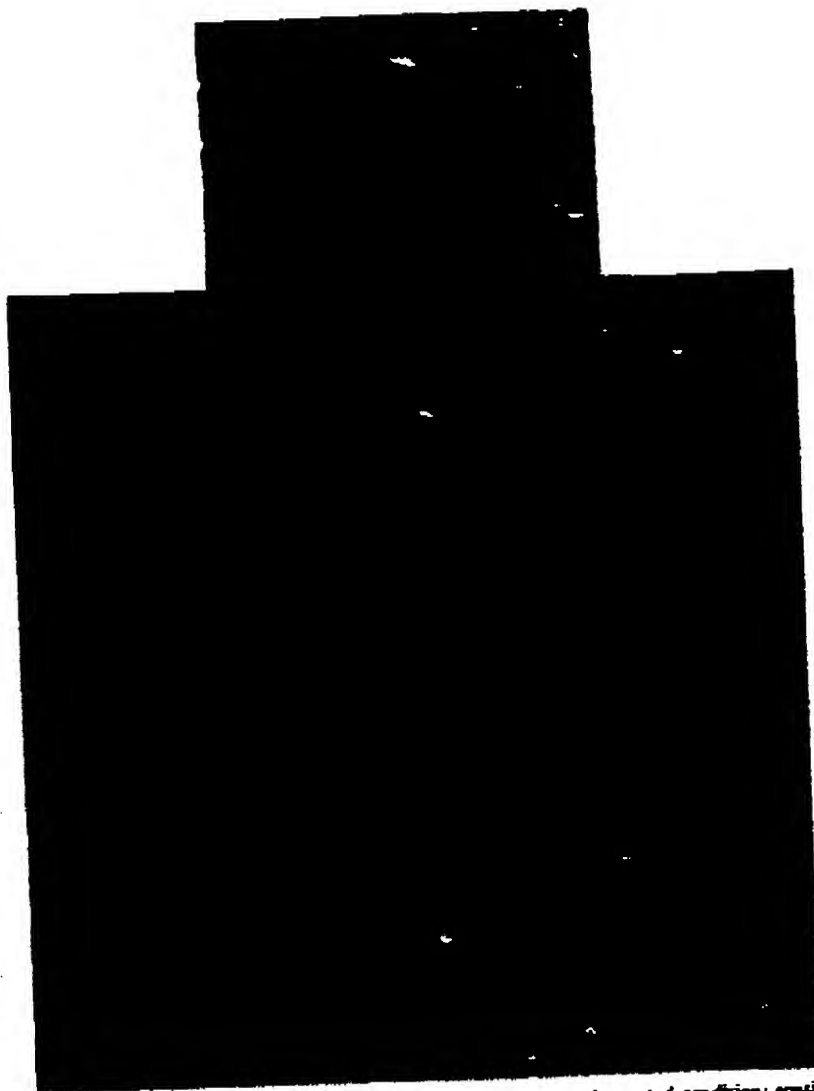
Fio. 2.   Electron backscatter and x-ray images of pack aluminized Mar-M200.   As-coated condition; coating cycle 2 hr at 1600 F.
(A) Electron backscatter image; (B) nickel; (C) tungsten; (D) aluminum; (E) chromium; (F) cobalt; (G) titanium.   250X.

examined in the various specified conditions, were left undisturbed since the areas of principal interest were the outer metallic and oxide layers.   A number of specimens were subjected to x-ray diffraction analyses of surfaces in the plane of the coating after stepwise removal of measured amounts of coating by electropolishing.

Hardness measurements of coatings and substrates were made with a Leitz microhardness tester using a Vickers diamond indentor under a 25-g load.   All samples were metallographically polished and etched prior to hardness testing.   Four hardness impressions were made on each area of interest, and readings from the eight diagonals were averaged to give a single hardness value.

RESULTS OF STRUCTURE AND COMPOSITION STUDIES

AS-COATED CONDITION

Figure 1 shows the microstructure of a specimen coated by pack cementation at 1600 F for 2 hr. Phase identities obtained from the results of the various analytical techniques, and the results of microhardness measurements are presented in the same figure.   EPM electron backscatter and x-ray images for the same specimen are shown in Fig. 2 and quantitative analysis data in Fig. 3.   Pertinent structure and composition features are as follows:

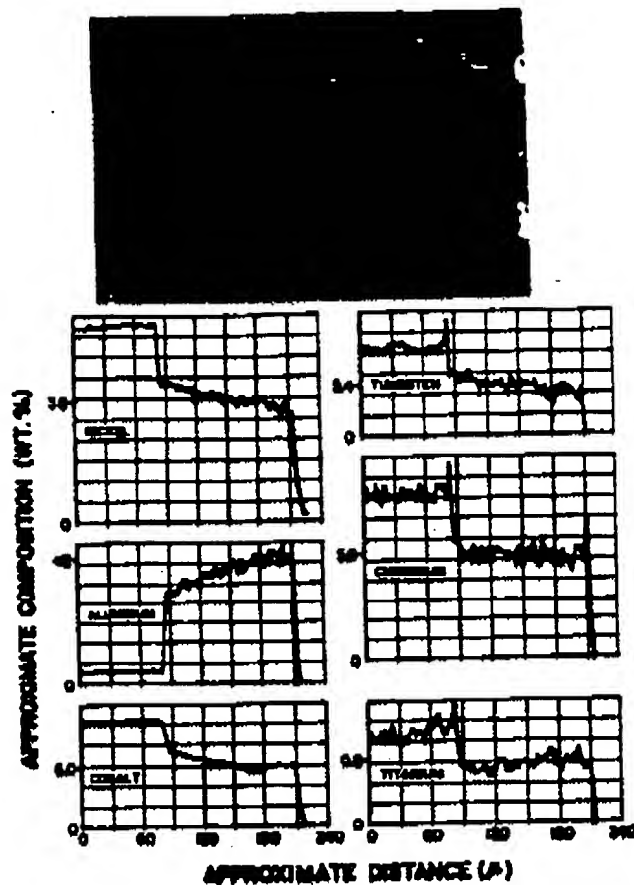The matrix of the outer surface layer of the coat-

Fig. 3.   Composition profiles of pack aluminized Mar-M200.   As-coated conditions; coating cycle 2 hr at 1,600 F.
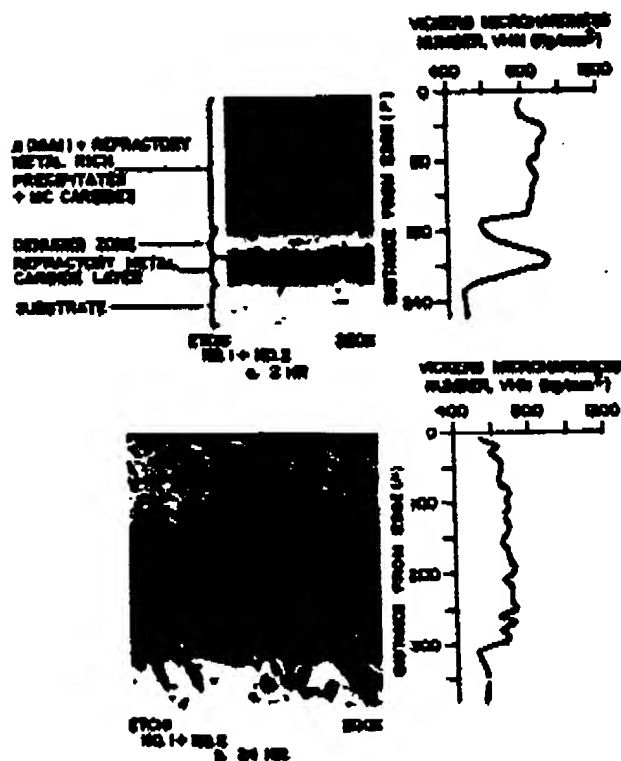

Fig. 4.   Microstructure, microhardness profiles and general phase identities for pack aluminized Mar-M200 after short-time heat treatment at 2200 F.   Original magnifications reduced 30% in reproduction.
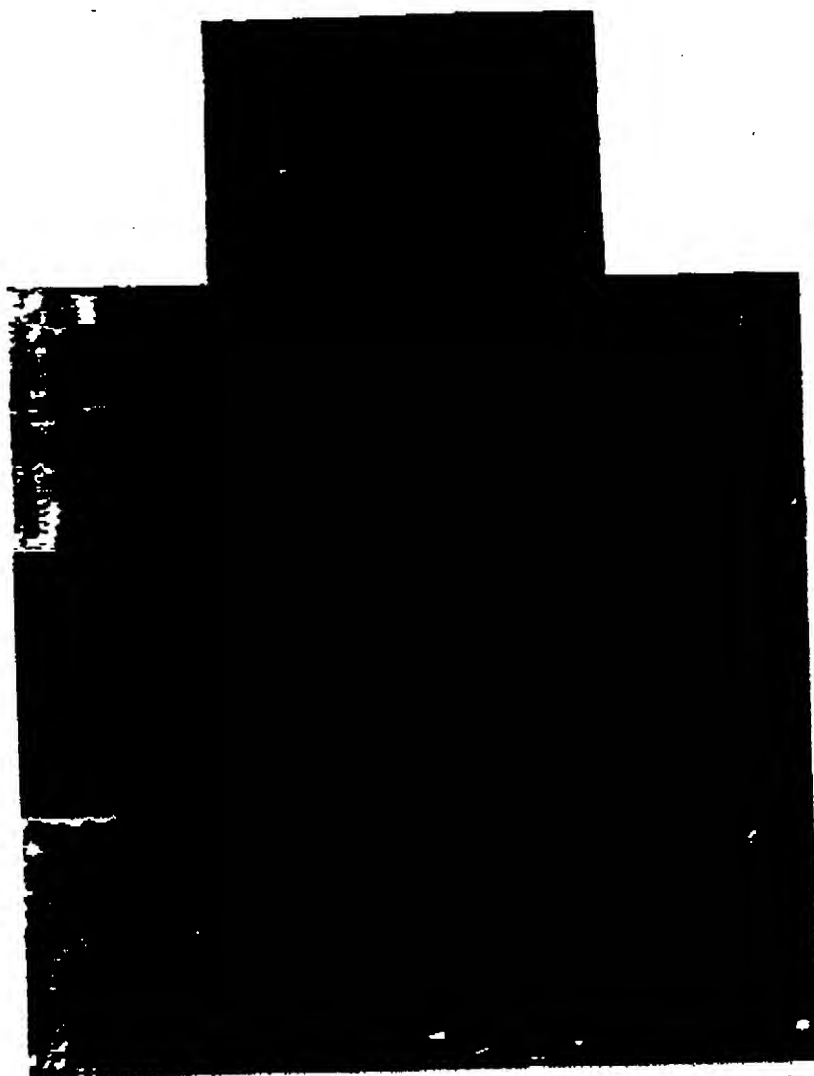
Fig. 5.   Electron backscatter and x-ray images of pack aluminized Mar-M200 after 2 hr at 2200 F.   (A) Electron backscatter image; (B) nickel; (C) tungsten; (D) aluminum; (E) chromium; (F) cobalt; (G) titanium.   250×.

ing is principally the δ(Ni₃Al₄) phase. Decreasing aluminum contents and microhardness values in the inner layers suggest a gradually increasing proportion of β(NiAl) phase to where this compound is the sole matrix phase abutting the γ + γ′ phases of the substrate. An expected layer of γ′(Ni₃Al) is either not present or is too thin to be detected by the analytical techniques used.

MC ([Ti,Nb,W]C) carbides (1), originally present in the matrix, are also present in the coating; these carbides occasionally extend, in discontinuous chains, up to the outer surface of the coating.

Fine precipitates, barely resolvable at 1500×, exist throughout the coating layer. Qualitative EPM indicates the presence of two discrete phases, one being rich in tungsten and the other in chromium. XRD analyses on a plane sectioned heat treated

specimen (Fig. 7) indicate that the tungsten-rich phase is metallic tungsten containing 10-15% chromium in solution and that the chromium-rich phase is apparently γ-nickel solid solution. EPM data indicates that all of the alloying element concentrations, when corrected for aluminum dilution, are essentially equal to their concentrations in the base alloy; i.e., that even though some of these elements have precipitated in the aluminum-rich matrix, they have effectively remained stationary in space during the coating process. Suggestions of nonuniform precipitation, manifested by vertical banding (Fig. 1), reflect interdendritic segregation of the refractory alloying elements, a condition known to be present in as-cast Mar-M200.

EPM x-ray images and scans for tungsten, chromium and titanium indicate a very thin (~2 μ)
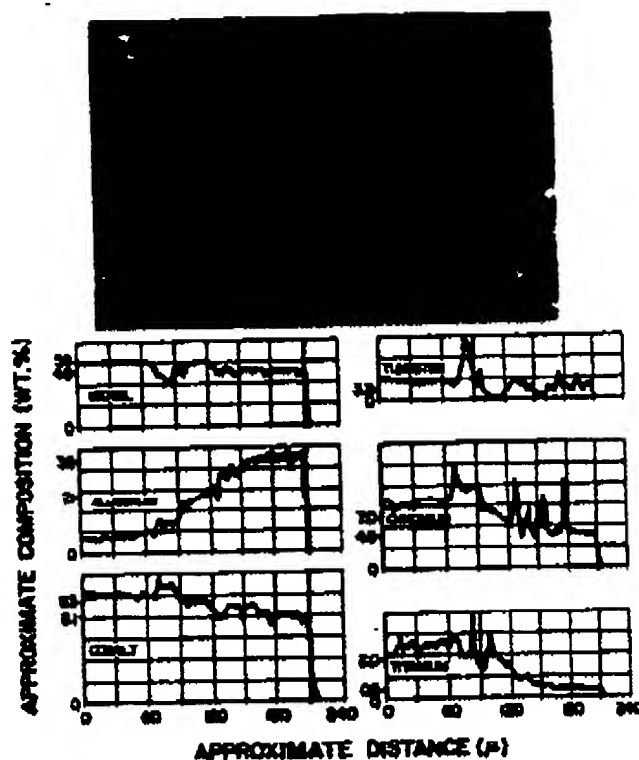
Goward, Boone and Giggins

Fig. 6.   Composition profiles of pack aluminized Mar-M200 after 3 hr at 2200 F.

layer of enrichment of these elements at the coating-substrate interface. This layer is barely discernible by optical microscopy and the phases present are as yet unidentified.

SHORT-TIME HEAT TREATED AND/OR OXIDIZED CONDITION

Figures 4, 5 and 6 summarize the information obtained for relatively short-time heat treatment and/or oxidized specimens of pack cementation aluminide coatings on Mar-M200. The effects of the atmosphere of heat treatment, neutral (argon) or oxidizing are essentially the same up to 24 hr. Significant changes occur as a result of diffusion interactions during these heat treatments as follows:

Short, high-temperature (2 hr, 2200 F) heat treatment converts the matrix of the coating from δ + β phases to the β phase; manifestations of this transformation are the reduction in both aluminum content and microhardness.

Refractory metal-rich (tungsten, chromium) precipitates in the β coating matrix coarsen with heat treatment; this is best illustrated by the increased fluctuations in the EPM scans for these elements (Fig. 6). Similar fluctuations occur in the microhardness profiles.

A zone, gradating from a region of lower precipitation density to essentially complete absence of pre-

cipitates (so-called denuded zone), appears as the result of heat treatment. This zone was found to contain essentially no tungsten and to have relatively low hardness.

Below the denuded zone, a complex layer consisting of a variety of hard particles develops. EPM scans indicate this layer to be heterogeneously rich in tungsten, chromium and to a lesser extent, titanium. Stain etching with alkaline potassium permanganate (Etch No. 2) reveals a variety of phases in this layer; the presence of at least three different types of carbides is suggested.

X-ray diffraction results from successively deeper planes in the coating, obtained by stepwise electropolishing of a specimen that had been oxidized for 24 hr at 2200 F, are presented with the corresponding planar microstructures in Fig. 7.

In the outer layer, Section A-A', α-tungsten particles containing up to 15% chromium in solution and γ-phase nickel solid solution particles containing large amounts of chromium were identified. The upper part of the denuded zone, Section B-B', is β phase containing a few α-tungsten particles. The bulk of the denuded zone is virtually pure β phase, free of second phase particles. The hard particle layer was determined to contain many phases; MC (probably TiC) and M₆C carbides were identified in the upper part of the layer while the η carbide M₆C was identified in the lower part
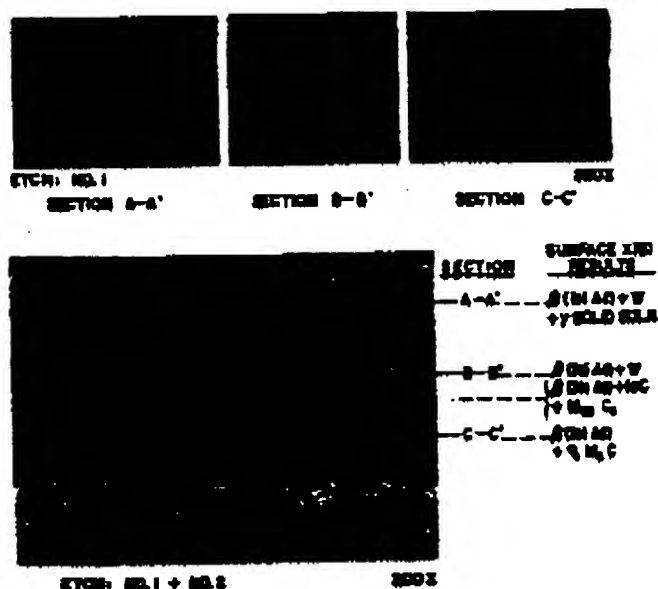
FIG. 7.   X-ray diffraction results for planar sections of pack aluminized Mar-M200 after 24 hr at 2200 F.   Original magnifications reduced 50% in reproduction.

FIG. 8.   Dissolution of MC carbides in aluminide coating evidenced by serrated edges of carbides.   1000×.

of the layer, Section C-C', and below.   The matrix in all planar sections was identified as the β phase.

The general effect of increasing time at temperature is illustrated in Fig. 4a and b.   Microhardness continues to decrease, the previously described phases become more pronounced and grain growth is in process.   Grain growth is initially inhibited by the grain boundary precipitates and subsequently accelerates as the precipitates dissolve.   Figure 8 illustrates what is believed to be the gradual dissolution of MC carbides in the coating layer with

heat treatment at 2200 F.   Such heat treatment has no observable effect on MC carbides in the substrate (1).

EXTENDED OXIDATION CONDITION

Figures 9 through 13 and Table 1 summarize typical structure and composition information on specimens of pack cementation aluminide coated Mar-M200 that have been oxidized for extended periods of time at 2200 F.

TABLE 1.   Composition of β and γ' Phases in Pack Cementation Coating on Mar-M200 Oxidized for 96 Hr at 2200 F

Element	β(NiAl) phase, wt %	γ'(NiAl) phase, wt %
Ni	69	69
Al	16	8.1
Co	7.1	10.5
W	1.3	7.2
Cr	5.7	10.4
Ti	1.6	3.1

The principal retained oxidation products are Al₂O₃ and NiAl₂O₄.

The fine tungsten and chromium-rich precipitates completely dissolved in the coating in a relatively short time (25–50 hr).

A thin layer of coating on the outer surface has been degraded in aluminum content to the γ nickel-base solid solution phase.   The next underlying layer is the γ' phase alloyed with cobalt, tungsten, chromium and titanium.

The middle, and thickest, layer of the coating consists of large grains of alloyed β interspersed with alloyed γ', the former decreasing and the latter increasing in amount with time at temperature.
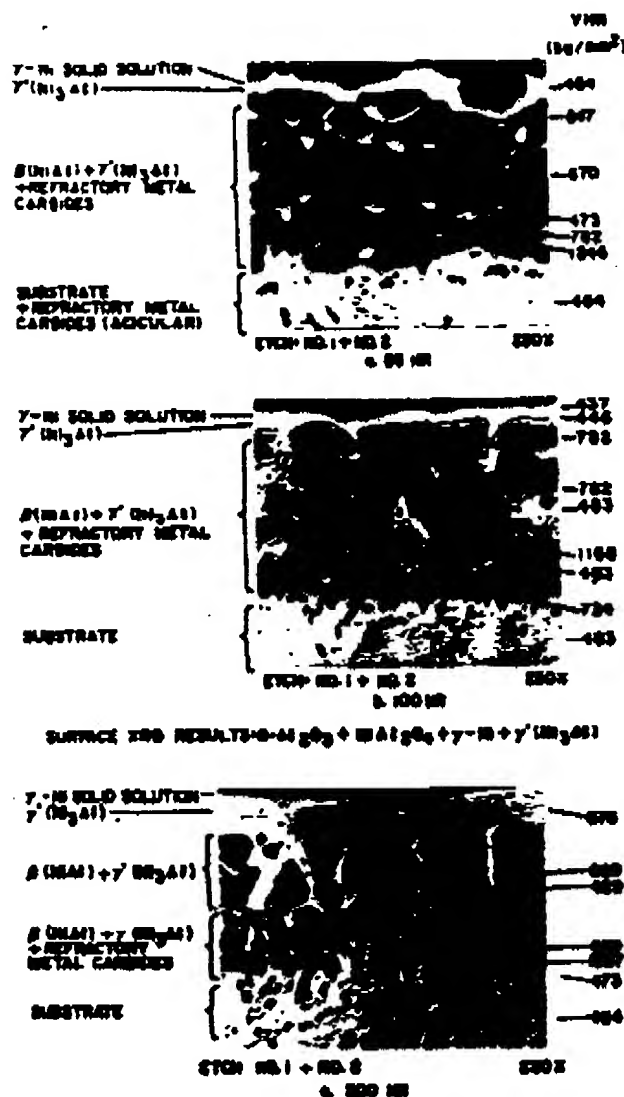
Goward, Boone and Giggins

Fig. 9.   Microstructures, microhardness data and phase identities for pack aluminized Mar-M200 after oxidation at 2200 F. Original magnification reduced 50% in reproduction.

Partition equilibrium of alloying elements has been attained between these two phases, with the γ' phase having the higher alloy content. The high partition of tungsten to this phase is worthy of note. A third phase, particularly evident in Fig. 9b and 10, consisting of small tungsten rich particles usually in the γ' field is also discernible in this layer of the coating. While this phase has not as yet been identified, its stain etching characteristics and high tungsten content suggest that it is also a carbide. The phase is no longer present after very long times (200 hr) at temperature; it is probable that it dissolves in the γ' phase.

The coating layer next to the substrate still contains a variety of hard phases, which have previously been identified as carbides, along with a

mixture of β and γ', with the latter phase predominating with extended time at temperature. The morphology of the carbide phases varies with time at temperature, as illustrated in Fig. 9a, b and c. EPM data suggests that the very large hard phase of the type shown in Fig. 9a and 10 is a M₆C carbide, containing W, Cr, Co and Ni.

An acicular phase, tentatively identified on the basis of EPM data and stain etching characteristics as an M₆C carbide containing substantial amounts of tungsten, forms under the coating in the substrate. The depth to which this phase is found increases with time at temperature, suggesting that it is formed as a result of inward diffusion of aluminum. EPM data on a specimen oxidized for 200 hr at 2200 F, Fig. 12, indicate that the aluminum content of the system
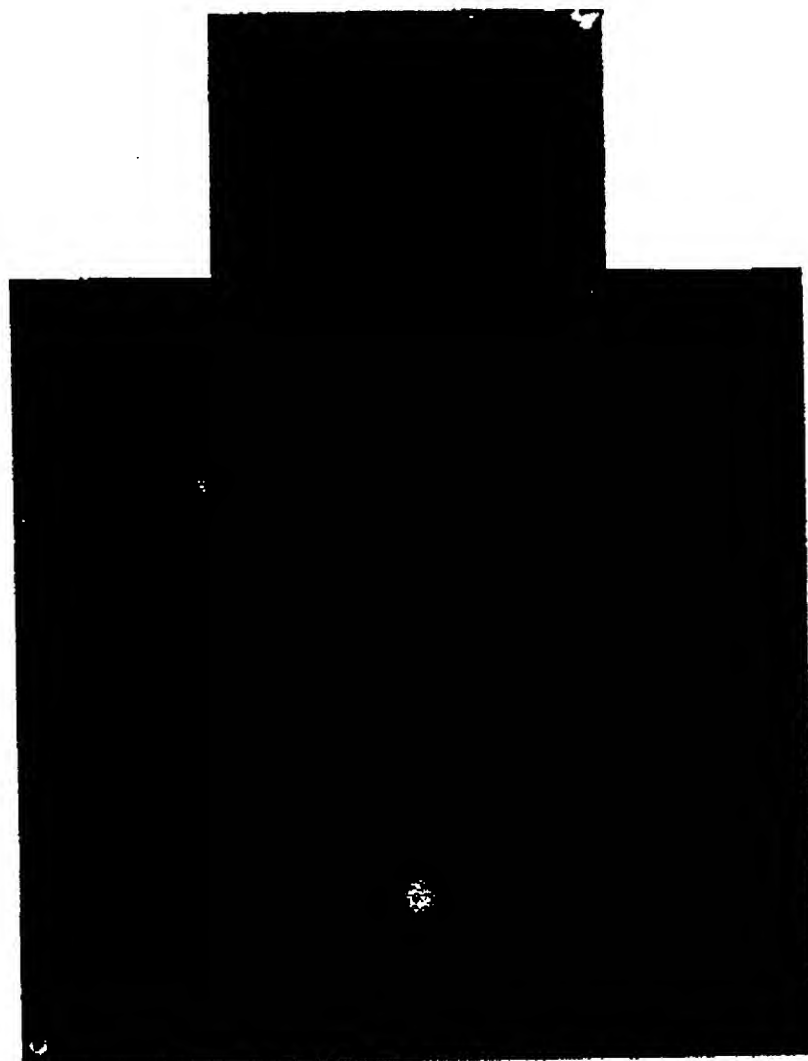
235

FIG. 10.   Electron backscatter and x-ray images of pack aluminized Mar-M200 after oxidation for 56 hr at 2200 F.   (A) Electron back; scatter image; (B) nickel; (C) tungsten; (D) aluminum; (E) chromium; (F) cobalt; (G) titanium.   250X.

decreases from 1½% at the inner surface of the β phase to 5%, the level normally present in the substrate, at a depth of 6 to 8 mils. An opposite gradient of tungsten concentration to the same depth is also apparent.

Further oxidation simply continues the progression of phase changes previously described. Figure 13 illustrates the typical appearance of a coating near the end of its protective life. The β phase has completely disappeared from the system; the remaining phases in progression from the surface are alloyed γ (nickel solid solution), alloyed γ' and alloyed $\gamma + \gamma'$ of the substrate. Remnants of refractory metal carbides remain in a discontinuous layer below the γ' layer. The particles have spheroidised and their appearance suggests that they are gradually dissolving; indeed, microstructures of

specimens oxidised for longer periods of time show that these carbides dissolve completely in the matrix.

DISCUSSION

COATING FORMATION

All aluminising coating processes operate by exposing the surface of the substrate alloy to a phase of higher aluminum activity than that of the base material. The surface phase of the coated alloy must necessarily have the same activity as the aluminum source phase of the coating medium, equilibrium conditions being assumed. For the present case, the indicated surface phase for the particular pack cementation mixture and temperature (1600 F) used is the δ (Ni_2Al_3) phase. The nature of the process of transfer of aluminum from
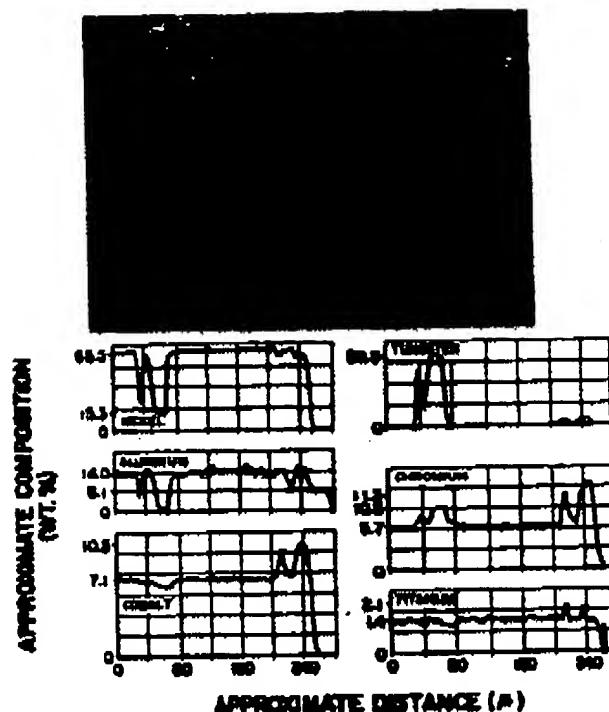
Goward, Boone and Giggins

Fig. 11. Composition profiles of pack aluminized Mar-M200 after oxidation for 85 hr at 2000 F.
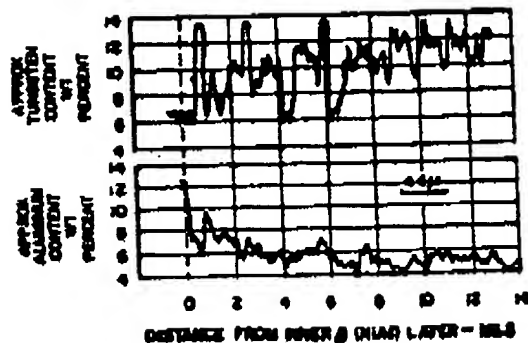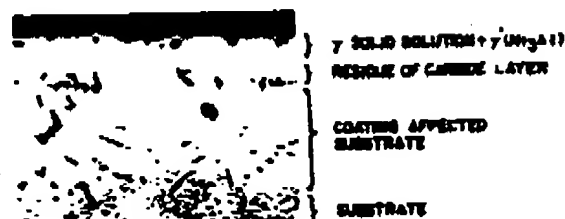

Fig. 12. Microstructure (250×) and EPM trace of aluminum penetration in pack aluminized Mar-M200 after oxidation for 200 hr at 2200 F. Original magnification reduced 30% in reproduction.

the pack medium to the alloy surface, while obscure, probably involves the formation of an aluminum chloride, by reaction of aluminum with HCl from calculation of the

Fig. 13. Microstructure and phase identities of pack aluminized Mar-M200 after extended oxidation to near the end of the protection life of the coating. 125×.

aluminum activity of this system is difficult, if not impossible, but it is apparent that this activity is equivalent to that of the observed surface phase, δ (Ni₂Al₃). Other surface phases will be observed for various different coating conditions. Decreasing the aluminum activity of the coating medium, for example by alloying the aluminum, will cause the formation of surface phases of lower activity such as the β (NiAl) phase. Surface phases of lower aluminum activity can also form as the aluminum activity of the pack mix decreases with time because of consumption of aluminum by coating formation, or depletion of the activator by volatilization.

The next important consideration is the nature of diffusion processes involved in the formation of the coating. Two limiting cases, inward aluminum diffusion and outward substrate element (predominantly nickel) diffusion and all combinations of these two cases are possible. The parameters that deter-

mine the nature of the diffusion processes are the activities and diffusion coefficients of aluminum and nickel (it will be demonstrated that the other major alloying elements are virtually stationary and are involved only secondarily in the diffusion processes).

Two natural markers, the MC [(Ti,W,Nb)C] carbides and the refractory alloying elements, allow a straightforward determination of the diffusing species for the system under study. Typical microstructures, illustrated by Fig. 2, indicate that MC carbides are present throughout the coating. EPM analyses of the major alloying elements (W,Cr,Co,-Ti), when normalized for aluminum dilution, indicate that these elements are present in the coating in the same proportion and concentration as in the substrate alloy. It is inconceivable that these elements could diffuse outward, all at the same rates, during the short, low-temperature coating cycle used. It must be concluded that this coating is formed by predominant inward diffusion of aluminum. Artificial marker experiments, involving the electrodeposition of a thin (5 μ) layer of nickel-Al₂O₃ on the alloy surface by entrapment electroplating and subsequent aluminising, confirmed this conclusion. Microscopic examination of the coating revealed that the artificial marker was on the outer surface of the coating at the completion of the aluminising process. While predominant inward aluminum diffusion occurs for this particular coating method, the reverse process, predominant nickel diffusion, and intermediate processes, can also occur for other coating conditions. This subject will be covered in more detail later in this discussion after other significant features of the coating are discussed.

The presence of the tungsten and chromium rich particles observed in the coating (Fig. 1, 2, 4 and 5) may be explained on the basis of limited solubility of these elements in either or both of the β and β-nickel-aluminum phases. The particles grow in size and persist during short-time heat treatments which convert the coating to single-phase β (NiAl). An explanation of the presence of α-tungsten particles based on limited solubility is in accord with the most recent Ni-Al-W phase diagram available.* Since available phase diagrams for Ni-Al-Cr (2, 3) are conflicting, the situation with regard to chromium solubility is not yet clear. The absence of α-chromium and the presence of γ-nickel solid solution suggests that chromium is present in high concentration in the latter phase. This is consistent with the co-existence of β and γ in the Ni-Al-Cr system (3).

The thin tungsten-chromium (and possibly titanium) rich layer at the coating substrate interface (Fig. 2 and 3) is a manifestation of the small but finite amount of outward nickel diffusion that must occur during coating formation. Since tungsten,

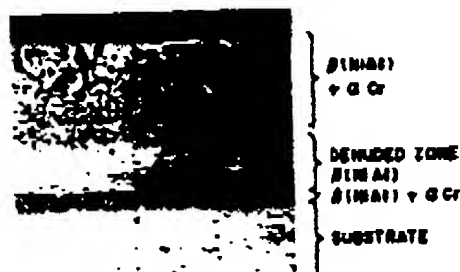* D. N. Duhl. The Nickel-Aluminum-Tungsten Phase Diagram. private communication.

Fig. 14.   Microstructure of pack aluminised Ni-20% Cr alloy, heat treated 4 hr at 2000 F.   250X.

chromium and titanium are virtually stationary at the low temperature of coating formation used, these elements must be enriched by nickel depletion on the substrate side of the interface. Such enrichment may be regarded as a precursor to the formation of the above described α-tungsten and chromium-rich γ-nickel solid solution phases.

The manifestations of outward nickel diffusion are more clearly illustrated during short-term air or inert atmosphere heat treatments in the range of 2000 to 2200 F. The high aluminum activity that caused predominant aluminum diffusion during the coating formation is now no longer present and so significant outward diffusion of nickel occurs, increasing in magnitude as the aluminum activity of the outer layers decreases with time. The original interface is at the plane of chromium-tungsten enrichment and the aluminum source is either the β (Ni₃Al₂) or hyperstoichiometric (aluminum-rich) β (NiAl) phase, depending on time. The products of the diffusion reaction are hypostoichiometric β (NiAl) above the original interface (denuded zone, Fig. 4a) and a band of refractory metal hard phases in a β (NiAl) matrix of still lower aluminum content, below the original interface and next to the substrate. The net result is illustrated in Fig. 4a, 5 and 6. The refractory metal hard phases have been tentatively identified as a mixture of carbides including MC, M₆C, and M₆C. The mechanism of formation of these carbides involves enrichment of tungsten (and titanium) and to a lesser extent chromium, as a result of nickel depletion, and subsequent or simultaneous reaction with carbon withdrawn from the substrate by outward diffusion from a depth necessary to supply the required amount of this element. Evidence of significant decarburisation in the form of denudation of carbides from grain boundaries to a depth of 4-6 mils has been observed in low carbon superalloys during similar coating processes. In carbon-free alloys, for example Ni-20% Cr, this layer consists of the α solid solution of the refractory alloying element as illustrated in Fig. 14.

Below the carbide layer, a thin layer of enrichment of cobalt and chromium is observed (Fig. 5 and 6). This layer must again be formed by nickel

Goward, Boone and Giggins

denudation and back diffusion of these two elements. Corresponding enrichment of tungsten and titanium is not observed, apparently because these elements are immobilized by carbide formation.

The alloy content of the β (NiAl) phase in the denuded zone, shown in Fig. 6, depends on time and temperature of the heat treatment. For the case illustrated, there has been negligible diffusion of tungsten, but significant diffusion of chromium and titanium into the zone as would be expected. The composition (low in tungsten) and absence of precipitates corresponds to the relatively low hardness in this region.

As previously mentioned, the relative diffusion rates of nickel and aluminum observed during the formation of this coating are specific for the particular conditions of coating medium composition and temperature used. The rates can be altered by changing either or both of the composition of the coating medium and temperature. For example, predominant outward nickel diffusion can be caused by the use of a coating medium of relatively low aluminum activity at a higher temperature. Figure 15 illustrates a coating formed at 2100 F from a pack cementation mixture using Ni₃Al₂ as the aluminum source. Predominant outward nickel diffusion is manifested by a relatively thick carbide layer and an outer NiAl layer free of secondary phases. EPM data indicate that the outer layer contains some cobalt, chromium and titanium in accordance with higher diffusion rates of these elements at the higher temperature used for coating formation. Tungsten concentration in the layer is vanishingly small because of its low solubility in the β phase and lower diffusion rate.

Initial work by Monson and Pollock (4) on the pack cementation aluminizing process for coating TD-nickel led to the conclusion that the outer layers of the coatings are formed by outward diffusion of nickel. This was deduced from the observation of a dense ThO₂ layer under the coating. This densification is the result of outward nickel diffusion which concentrates the ThO₂ in a layer. Several conditions lead to predominant outward nickel diffusion in the particular method used to coat TD-nickel. The most important of these are the high nickel activity of unalloyed TD-nickel, the low (1-5%) aluminum contents of the coating media and the higher temperatures used for coating formation. It is interesting to note that void formation occurred in these coatings on TD-nickel. Presumably the voids are formed by condensation of vacancies produced by outward diffusion of nickel. Void formation appears to be enhanced by the presence of the ThO₂ particles in TD-nickel; it still occurs, but to a lesser extent in unalloyed nickel. Although the possibility of void formation in highly alloyed systems cannot be ruled out, it has not yet been found in any of the systems observed in the present study.
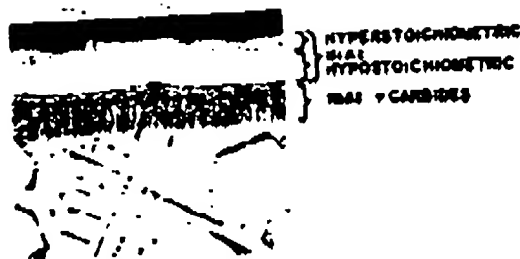

Fig. 15. Microstructure of coating formed by outward diffusion of nickel. Pack medium 15% Ni₃Al₂, 3% NH₄Cl, 82% Al₂O₃. Coating cycle 6 hr at 2100 F. 250×.

From the above considerations it follows that any of the total spectrum of possible diffusion processes between the two extremes of predominant nickel and predominant aluminum diffusion can be caused to occur by variation of the coating medium and temperature. In addition, predominant inward aluminum diffusion followed by increasing degrees of outward nickel diffusion can occur during a single step coating process if the aluminum activity of the coating medium decreases with time at temperature by consumption of either or both of the aluminum and the activator.

The mechanisms described are adequate to account for the variety of microstructural features observed in contemporary nickel-base superalloy aluminide coatings synthesized by several variations of the pack cementation method. Composition, and to a lesser extent, morphology of the secondary phases (carbides, etc.), produced by the diffusion processes will differ for each particular nickel alloy in accordance with its alloy content and microstructure. Minor secondary element additions such as silicon or chromium, to the coating medium may produce minor alterations in composition and structure but the above principles will still apply. In addition, the same mechanisms will apply for all other coating processes, such as hot dipping, slurry methods, vapor deposition (both chemical and physical), fused salt electrolysis, flame or plasma spraying, etc., that cause reactions of aluminum or aluminum-rich materials with the surfaces of alloys at elevated temperatures.

Another effect of short-term heat treatment, which carries over into long-term oxidation heat treatment is the dissolution of MC carbides in the aluminum-rich coating Fig. 8. Physical metallurgy studies indicate that MC carbides in Mar-M200 dissolve rapidly in the alloy over a temperature range of 2260 to 2450 F, whereas they are stable and do not dissolve in the range of 2000 to 2260 F during short-term heat treatment (1). The mechanism of the observed dissolution in the aluminum-rich coating in the range of 2000 to 2200 F has not been studied to any great extent. It has been observed that dissolving carbides are surrounded by what is apparently γ' phase, contained in the β-phase coating.

This suggests that the driving force for dissolution is appropriate substitution of the carbide elements (Ti, Nb, W and C) in, and resultant stabilization of, the γ' structure.

COATING DEGRADATION

Under idealized conditions, pure nickel-aluminum alloys in the β and $\beta + \gamma'$ region oxidize according to a parabolic rate law to form a protective layer of Al_2O_3.* The Al_2O_3 layer, however, has a tendency to spall under thermal cycling conditions such as those used during this study. In a practical, highly alloyed system, represented by the subject coating, the primary oxide initially formed is also Al_2O_3. The spalling tendency persists in this system with the result that aluminum is depleted from the coating at a greater rate than would be predicted for isothermal conditions. At some point, determined by the particular oxidation conditions, insufficient aluminum is present at the coating-oxide interface to cause singular formation of Al_2O_3. More complex oxides, such as the spinel $NiAl_2O_4$ and NiO, form and the depletion rate of aluminum increases because of higher mass transport rates in these oxides than in Al_2O_3. The net result of depletion of aluminum from the coating is a reversal of the original coating process with the progressive formation of phases lower in aluminum than the original β phase. Figure 9 and 13 illustrate this progression with time; the relative amounts of γ and γ' phases increase at the expense of the β phase. During this process, a complex and incompletely understood three-phase ($\beta - \gamma' - \gamma$) system exists in the coating. The bulk of the alloying elements tend to partition to the γ' and γ phases.

The mechanism of nucleation and growth of the γ' phase in the β phase in a roughly columnar morphology (Fig. 9) during degradation is obscure. Ideally, a continuous layered structure of γ, γ' and β, sequential from the surface inward, should be observed. Approximations to this idealized structure have been observed in this study during degradation of systems of lower alloying element content. Pure nickel, aluminized and oxidized, even more closely approximates the ideal structure. These observations suggest that nucleation of the γ' phase in the highly alloyed coating on Mar-M200 occurs preferentially in those regions rich in alloying elements. Such regions can be the refractory metal-rich precipitates observed at grain boundaries in the outer coating layer. Additional localized enrichment is caused by interdendritic segregation during casting of the alloy and is reproduced in the coating since in this case the coating is formed by predominant inward diffusion of aluminum.

Tungsten-rich particles, probably M_6C carbides, form in the highly alloyed γ' regions, as illustrated

*F. S. Pettit, Oxidation Mechanism for Nickel-Aluminum Alloys at Temperatures Between 900 and 1300 C, submitted for publication in Trans AIME.

in Fig. 9 and 10. These particles and the carbides of the refractory metal carbide layer at the coating substrate interface tend to spheroidize and eventually dissolve with time at temperature. MC carbides, originally present in the coating, dissolve completely within about 50 hr at 2200 F.

The end result of the degradation process is illustrated in Fig. 13. The β phase has been completely consumed and the system consists of an alloyed γ layer on the surface with the $\gamma - \gamma'$ structure of the substrate beneath. The γ' particles of the substrate have coarsened as a result of the prolonged heat treatment at elevated temperature.

Because of the highly alloyed multiphase nature of the coatings, spurious side reactions, such as localized accelerated attack, are to be expected and are indeed observed from time to time. Since these are random processes, differing in frequency and character for each coating alloy system, they will not be further discussed in this paper.

Loss of aluminum from the coating by inward diffusion to the substrate is small in comparison to surface loss for this system. An approximate estimate, based on the data presented in Fig. 12 is that about 10% of the aluminum content of a 3-mil coating is lost to the substrate by diffusion in 200 hr at 2200 F. The magnitude and importance of this loss of aluminum will, of course, increase exponentially with temperature. The major microstructural manifestation of inward aluminum penetration in this system at the temperature studied is the precipitation of an acicular tungsten-rich carbide phase in the substrate.

As with coating formation, the above described mechanisms of degradation are adequate to explain in a general manner, the oxidative degradation of most, if not all, aluminide coating-superalloy system. The major process is simply oxidation of a β (NiAl) matrix. The process proceeds at different rates for different coating-alloy systems and different oxidation conditions. Conditions that enhance the removal of Al_2O_3 (and other secondary oxides) from the surface will accelerate the degradation processes. Additions that decrease the spalling tendency of Al_2O_3, and perhaps also promote its formation in preference to other possible secondary oxides, will slow the degradation process.

SUMMARY

Studies of a model coated superalloy system, consisting of a pack cementation aluminide coating on Mar-M200, have established typical mechanisms of formation and oxidative degradation of such systems.

In this specific model, the coating is formed by predominant inward diffusion of aluminum and thus the coating incorporates many of the compositional and structural features of the substrate alloy. Short-term heat treatment at 2200 F, in the absence of the high aluminum activity present during the

Goward, Boone and Giggins

initial formation of the coating, causes increasing outward diffusion of nickel and correspondingly decreasing inward diffusion of aluminum at the original coating-substrate interface. Enrichment of refractory alloying elements caused by the resulting nickel depletion causes formation of a layer of refractory element carbides at the coating-substrate interface. More generally, it follows that coating formation can occur by predominant inward aluminum diffusion, predominant outward nickel diffusion or by any of all possible combinations of these two limiting cases depending on the relative activities of aluminum and nickel in the coating medium-alloy system. The major oxidation-resistant layer of such coatings is primarily the β (NiAl) phase, modified according to the particular coating method used.

Aluminide coatings are protective by virtue of formation of a surface layer of aluminum oxide during oxidation. Thermal cycling causes spalling of this oxide and the system degrades by removal of aluminum from the coating as required to re-form the oxide layer. The coating thus reverts sequentially from NiAl to NiAl + Ni₃Al, Ni₃Al + Ni solid solution and finally to a single layer of nickel solid solution over the substrate alloy. The latter phases tend to form oxides that are less protective than aluminum oxide and the system eventually reverts to oxidation in a manner characteristic of the uncoated alloy. The rate of degradation is dependent on specific oxidation conditions and will also be moderately different for each specific coating-alloy combination but the general principles will still apply for purely oxidative processes.

REFERENCES

1. B. J. Piearcey and R. W. Smashey. The Carbide Phases in Mar-M200, accepted for publication in Trans AIME, April (1967).

2. I. I. Kornilov and R. S. Mints. Phase Diagram of CrNi - NiAl System, Izvest Sektora Fiz-Khim Analiza, Inst Obshchei i Neorg Khim. Akad Nauk SSSR. 23 (1953) 111.

3. A. Taylor and R. W. Floyd. The Constitution of Nickel-Rich Alloys of the Nickel-Chromium-Aluminum System. J Inst Metals. 81 (1953) 451.

4. L. A. Moncton and W. I. Pollock. Development of Coatings for Protection of Dispersion Strengthened Nickel from Oxidation. AF33(615) 1704. Second Quarterly Progress Report. January 15 (1965) 175.

Abstracts Invited for -
ASM Metal Science Forums

"Criteria for Brittle Crack Extension"
"Superplasticity"

Abstracts of 250- to 300-word length are being invited by the ASM Transactions Committee for its Metal Science Forums to be held in Cleveland during the Society's 1967 National Metal Congress and Exposition. "Criteria for Brittle Crack Extension" is scheduled for October 16, "Superplasticity" for October 17.

Each Forum will be of day's duration. The morning session will be devoted to a keynote paper and to discussions (invited and from the floor) of the subject, the afternoon session to abstracts on the same general subject.

Due date for abstracts is July 17. Abstracts for presentation at these Forums should be addressed to the appropriate Metal Science Forum, c/o Editor, Transactions Quarterly, American Society for Metals, Metals Park, Ohio 44073, U.S.A.

Current Research
on the Surface Protection of Superalloys
for Gas Turbine Engines

'36169

by G. W. Goward

INTRODUCTION

The two major requirements for nickel and cobalt-base superalloys for use in the hot section of the aircraft gas turbine are high strength and resistance to surface degradation. Over the past decade, increasing turbine inlet temperatures, with the corresponding increase in metal temperatures, have caused a renewed interest in the problem of maintaining surface stability of these alloys over long periods of time. This paper describes our current understanding of the mechanisms of surface degradation, and also deals with recent research leading to more resistant materials. To bring some focus to the discussion nickel-base materials are used as models; brief references to the parallel behavior of cobalt-base alloys are made where appropriate.

Exact definitions of the environmental conditions in the hot section of the gas turbine engine can lead to great complexity. However, for the purposes of this paper this environment can be rather simply defined as a high velocity, high pressure, hot gas stream which is quite generally oxidizing toward the materials of interest. Further, this gas stream may fluctuate in temperature (heat flux) over wide ranges, and may, under certain conditions, contain a variety of inorganic salts (Na, Ca, Mg, etc.) introduced by a variety of sources. From this definition, three major factors contributing to the surface degradation of turbine materials can be defined. These are oxidation, thermal fluctuations, and hot corrosion. Interrelations among these will become apparent in the text which follows.

HISTORICAL

Very simply stated, to the oxidation researcher the history of nickel-base superalloys is one of a gradual progression, over a period of about 30 years, from essentially Ni-20% Cr alloys to what may be considered as essentially Ni-Cr-Al alloys with a variety of other elements added for strengthening purposes. In contrast, the oxidation base of cobalt

alloys, Co-20 to 25% Cr, has persisted, with the only known exception being the AiResist series of alloys, wherein aluminum has been added for increased oxidation resistance.

This is illustrated in Table I which presents a summary of the "old" and the "new". The most interesting observation to be made about these data is the gradual decrease in chromium content of the alloys and the sometimes halting, but definite increase in aluminum content. From the viewpoint of the metallurgist it is clear why this has happened—to achieve ever higher strengths at higher temperatures. It is interesting, however, to note the composition of the last nickel-base alloy in Table I; chromium content has been increased and aluminum content has been decreased. It might be concluded that the alloy designer was seriously thinking of environmental effects when this alloy was formulated.

For much of the remainder of this discussion, reference will frequently be made to "Cr_2O_3 formers" and "Al_2O_3 formers". Referring again to the compositions in Table I the basic significance of these terms should be immediately apparent.

OXIDATION

Pure metals derive their resistance to a high temperature oxidizing environment by the formation of protective oxide scales. If all goes according to theory, these scales grow at a rate which decreases with time, in many cases according to a parabolic rate law. The great majority of practical systems are, however, highly alloyed and the important oxidation process in what is generally termed "selective oxidation". This simply means that, considering the thermodynamics of oxide formation, one of the elements of these alloys is selectively oxidized to form its oxide, to the exclusion of formation of oxides of those metals with lesser affinity for oxygen. If the alloy is designed properly, the desired oxide forms as an external scale instead of a generally undesirable internal subscale.

All other things being equal, it is preferred that the protective oxide increase in thickness at the lowest possible rate. Since the growth rates of these thick films are governed by diffusion of one or more

G. W. GOWARD is Research Supervisor of Oxidation and Coatings, Advanced Materials Research and Development Laboratory, Pratt & Whitney Aircraft, Middletown, Conn. Paper presented at the 36th ... 10, 1970.
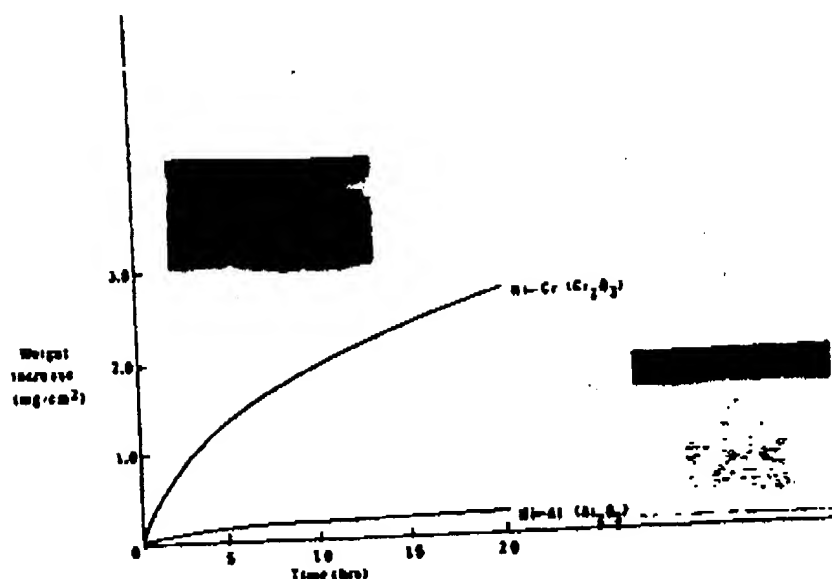
Fig. 1—Comparison of rates of growth of Al_2O_3 and Cr_2O_3 protective scales on Ni-Al and Ni-Cr alloys respectively at 2100°F. Photomicrographs (1000X reduced to 50% of original size) illustrate the substantially thicker oxide scale grown on the Ni-Cr alloy.

species through the films, it might be concluded that the preferred oxides could be selected on the basis of first principles from diffusion data. This is indeed possible, but to illustrate the principles in a more straightforward and practical manner it is more convenient to consider the relative isothermal oxidation rates of two pure, but approximately practical systems. Fig. 1 indicates the relative rates of formation of Cr_2O_3 on a nickel-chromium alloy and Al_2O_3 on a nickel-aluminum alloy. As could have been predicted from basic diffusion information, the Al_2O_3 scale grows at a substantially lower rate.
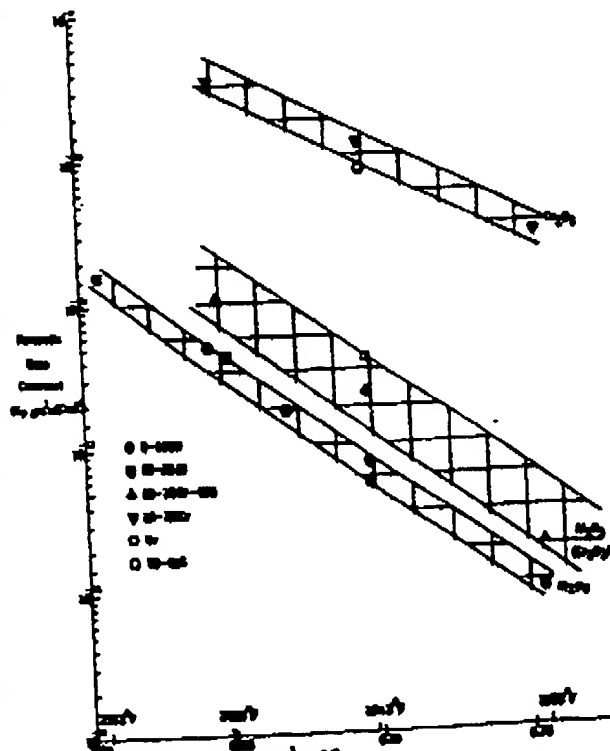
This behavior is more extensively illustrated in Fig. 2 which compares parabolic rate constants[*] for a number of Al_2O_3 formers and Cr_2O_3 formers. In addition to the obvious advantages of the Al_2O_3 formers, there are other interesting points illustrated. First, Al_2O_3 forms at a significantly higher rate on the Ni-Cr-Al alloys than on Ni-Al alloys. It is believed that this is caused by a small but significant doping of Al_2O_3 by chromium, which apparently increases the transport rate in the Al_2O_3.

Second, the anomalously low rate of Cr_2O_3 formation on TD NiC (thoria dispersed Ni-30% Cr) is apparent. It has been found from marker experiments that the direction of growth of Cr_2O_3 on TD NiC is apparently different than that on Ni-30% Cr. On Ni-30% Cr, the oxide grows in an outward direction, while on TD NiC the oxide apparently grows inward. Marker experiments must be interpreted with great care; it is clear, however, that the presence of the thorium oxide particles in the alloy has substantially altered the oxidation mechanism.

It is also significant to note in Fig. 2 that the commercial alloy B-1900 appears to behave as if it were an Al_2O_3 former.

Thus, it seems that Al_2O_3 formation is desirable. It may well be asked if Cr_2O_3 formation is not good enough. The answer depends on the environmental conditions imposed. For instance, one problem with Cr_2O_3 is illustrated in Fig. 3, which compares the oxidation behavior of TD NiC under static and dynamic gas conditions. The dynamic condition in this case was a high velocity (500 fps) isothermal gas stream. While both the laboratory cyclic and isothermal oxidation behavior of the alloy appear quite promising, the behavior of the alloy under dynamic conditions is less so because of the enhanced volatilization of Cr_2O_3 (as CrO_3) in the high velocity gas stream.

[*] K_p from the expression $\left(\frac{\Delta m}{A}\right)^2$ ... where $\frac{\Delta m}{A}$ = weight ... (mg/cm^2) and t = time interval in seconds.

Table I—Typical superalloy composition

|	C	B	Zr	Ni	Co	W	Ta	Mo	Ti	Cr	Al	Other
Nickel-Base												
Hastelloy X[w]	0.10	---	--	Bal	1.5	0.6	---	9.0	---	22	---	18.0Fe
Nimonic 80[w]	0.10	---	--	Bal	2.0	---	---	---	2.5	20	1.3	---
Waspaloy[w]	0.08	0.006	0.06	Bal	13.0	---	---	4.3	3.0	20	1.3	---
IN-100[c]	0.18	0.014	0.06	Bal	15.0	---	---	3.0	4.7	10	5.5	1V
MAR-M200[c]	0.15	0.015	0.05	Bal	10.0	12	---	---	2.0	9	5.0	---
B-1900[c]	0.10	0.015	0.10	Bal	10.0	---	4.0	6.0	1.0	8	6.0	---
IN 738[c]	0.17	0.010	0.10	Bal	8.0	2.6	1.7	1.7	3.4	16	3.4	0.9Cb
Cobalt-Base												
X-40[c]	0.50	---	--	10.0	Bal	7.5	---	---	---	25	---	---
WI-52[c]	0.45	---	--	---	Bal	11.0	---	---	---	21	---	2.0Cr
MAR-M302[c]	0.85	0.005	0.20	---	Bal	10.0	9.0	---	---	21	---	0.1Y
AiResist 13	0.45	---	--	---	Bal	11.0	---	---	---	21	3-5	2:0Cb

w = wrought

c = cast
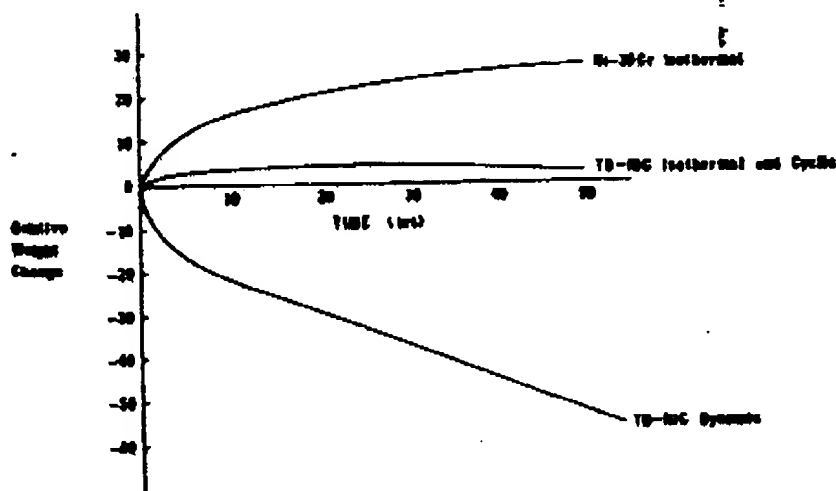
Fig. 3—Comparison of static and dynamic oxidation of TD-NiC at 2000°F.

It is frequently proposed that alloys be designed to form spinel oxides. First principle calculations, however, indicate that it is very difficult to design an alloy to form a spinel as the sole protective oxide. For example, such calculations show that to form the spinel NiCr₂O₄ on a Ni-Cr alloy, the chromium activity in the alloy must be of the order of 10^{-4} to 10^{-5}. This activity corresponds to concentrations of chromium in the parts per million range. Under these conditions, external scale formation would not occur, but rather a nonprotective spinel subscale would form internally in the alloy. For most cases where spinel formation is observed on practical alloys, other oxides are present and it must be concluded that in these cases, with very few exceptions, spinel formation is purely accidental and is probably not beneficial. The formation of a manganese-chromium oxide spinel on Ni-Cr-Mn alloys is one of the few excep-

It is concluded, and this may be criticized as constituting a rather puristic point of view, that for the ultimate in high temperature oxidation resistance, superalloys should be designed so that Al₂O₃ is the sole protective oxide formed. More will be said later about how this should be done; at this point it is useful to illustrate the practical and not so puristic benefits to be gained thereby. Fig. 4, which compares the behavior of B-1900 and Hastelloy X, clearly shows the enhanced oxidation resistance gained by Al₂O₃ formation under both isothermal and so-called rig oxidation-erosion (high velocity gas stream plus thermal cycling) conditions with an alloy that contains substantial amounts of aluminum. This is not to say that the oxidation resistance of the particular alloy illustrated was designed from first principles—the alloy does form other oxides besides Al₂O₃—but it is probable that the alloy designer in this case did
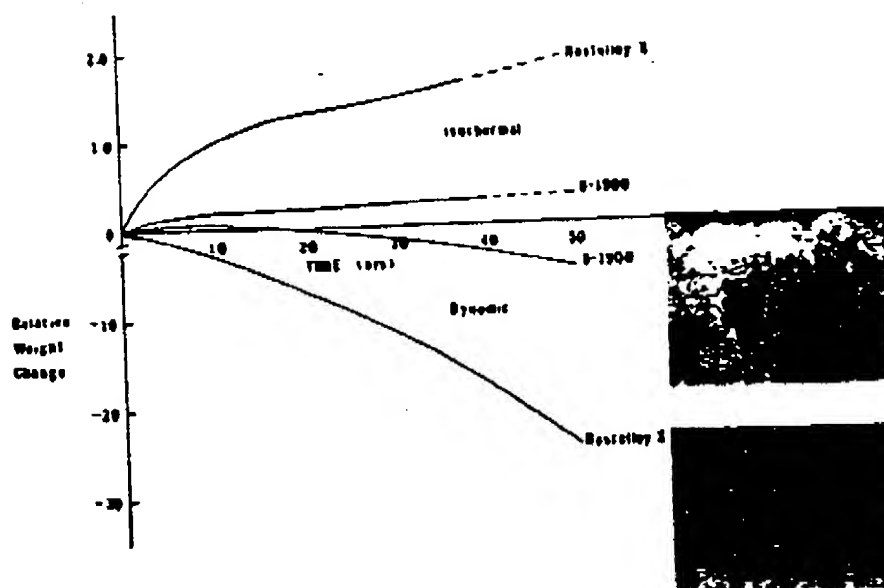
Fig. 4—Comparison of isothermal and cyclic-dynamic oxidation behavior of B-1900 and Hastelloy X at 2000°F (insets 250X reduced to 50% of original size).

have some idea as to what was taking place. It should also be stated that Hastelloy X does have its place in the scheme of things; it exhibits practically useful oxidation resistance up to 1800°F. For applications above this temperature it is coated with a material that forms Al_2O_3 as the protective oxide.

The first principles which can now be used to design nickel-base alloys which form protective Al_2O_3 scales are illustrated in Fig. 5, which shows the various oxides formed on alloys in the Ni-Cr-Al ternary system. Only the 2000°F isotherm is shown; the oxidation behavior of certain of the alloys is moderately temperature dependent. Binary Ni-Al alloys with Al contents above 15% form Al_2O_3;[2] below this value combinations of internal and external oxidation occur. Binary Ni-Cr alloys with Cr contents greater than about 15% form Cr_2O_3;[2] below this value internal and external oxidation occur. The most important fact is that minor additions of chromium allow external Al_2O_3 scales to form at much lower concentrations of aluminum than that required for the binary Ni-Al system. Basic reasons for this behavior are the subject of current research at Pratt and Whitney Aircraft and probably elsewhere. Considering that 5-6% aluminum is an appropriate concentration of aluminum in a superalloy for γ' formation, it is apparent that the very minimum chromium content required is in the range of 4-5%. The next step necessary to enable rational design of oxidation resistant, high strength alloys requires understanding of the effects of other alloying elements, such as W, Mo, Ti, and Ta, which are normally added to promote strength, on this oxidation behavior. Such studies are in progress. It is expected that W and Mo will be found to be neutral and Ti will be deleterious; no basis exists for predicting the effects of Ta.

oxidation accelerates surface degradation. Under practical conditions, superalloy turbine parts are subjected to a variety of thermal cycling conditions, the net result of which is thermally induced spalling of the protective oxide. On the next cycle the oxide must re-form, spall again, and so on. This repeated cycle depletes the surface of the alloy of aluminum (as reflected by weight loss) at a much faster rate than occurs under isothermal conditions. At some point in composition, which can now be fairly accurately predicted, insufficient aluminum will be present to form Al_2O_3 as the sole oxide, and other less protective oxides such as Cr_2O_3, spinels, NiO, etc. will form. The formation of these oxides can also be accompanied by internal oxidation of compositions containing relatively low aluminum concentrations.

Means of achieving further improvement in the cyclic oxidation performance of an Al_2O_3-forming nickel alloy appear to be tantalizingly simple; that

THERMAL FLUCTUATIONS

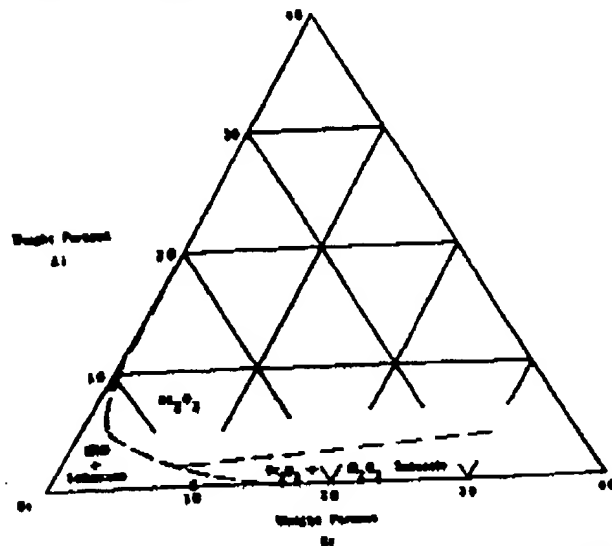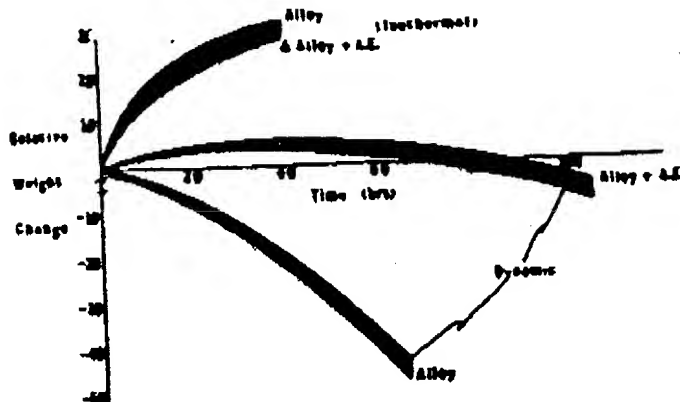... consider the second major surface degradation ...

Fig. 5—Oxide scales formed on various alloys in the ternary Ni-Cr-Al system at 2000°F.

Fig 6—Isothermal and dynamic-cyclic oxidation of Ni-Cr-Al alloy illustrating oxide adherence gained by addition of an active element (yttrium).

that the oxide should be made more adherent. As is now fairly well known, this can be done by minor modifications of alloy chemistry, although the fundamentals of the process are not well understood. Fig. 6 shows the beneficial effect of promoting increased oxide adherence on an Al_2O_3-forming Ni-Cr-Al alloy by the addition of a fraction of a percent of an active metal. The isothermal oxidation behavior of the alloy is not significantly changed but the cyclic oxidation behavior is markedly improved. The reactive element involved in this case is yttrium—similar effects can be obtained with other Group IIIB elements and many of the rare earths.

This general phenomenon has been known for many years, particularly for iron-base alloys,[ ] but it is only recently that its importance in Al_2O_3-forming nickel and cobalt-base alloys has been fully appreciated. Because basic understanding of the oxide-metal interface is at a relatively low level, the mechanism by which oxide adherence is enhanced by active element additions is the subject of considerable controversy. A variety of mechanisms including macro-pegging by internal oxides, graded seal effects, modification of mechanical properties of the oxide scale, vacancy sink effects, and enhanced atomic bonding have been proposed to explain the enhanced oxide adherence observed. By a process of elimination, involving detailed microstructural studies of the metal-oxide interface, the latter mechanism, that is, enhanced atomic bonding across the metal-oxide interface, seems to be the most logical. This conclusion is quite tentative at this time and a great deal of research remains to be done to explain this intriguing and highly practical behavior. It is believed that this general subject constitutes the most important type of oxidation research that can be done on this class of alloys.

Active development of practical alloys based on the principles of Al_2O_3 formation and enhanced oxide adherence is now in progress. Low alloy content, polycrystalline sheet alloys based on the Ni-Cr-Al-Y composition, are in the advanced stages of development and will be reported on in detail in the near future. To date, the fractional percentages of yttrium required to promote enhanced oxide adherence have been found to cause no deleterious mechanical property effects in these moderate strength wrought, polycrystalline nickel

base alloys, the story is not so encouraging; additions of yttrium and similar active elements have been found to seriously degrade creep-rupture properties.[ ] Fortunately, the recently developed single crystal technology[ ] for nickel-base superalloys provides a solution to this problem; additions of yttrium and other reactive metals to properly designed single crystal alloys cause no significant degradation of creep properties. Specific single crystal alloys based on Ni-Cr-Al-Y compositions with Ta, W, Ti etc. strengthening additions will also be reported on in detail in the near future.

As previously mentioned, most contemporary cobalt-base superalloys rely on the Co-20 to 25% Cr base composition for oxidation and hot corrosion resistance. Since aluminum does not contribute to strengthening on these alloys, as it does in nickel-base materials, there has been no great impetus on the part of alloy developers to add significant amounts of this element to cobalt alloys. The recently developed AiResist alloys (Table I) are the exception. These alloys tend to be Al_2O_3 formers and it is fully expected that more Co-Cr-Al-Y base alloys will appear as basic research progresses to define optimum compositions in the system.

HOT CORROSION

The third major factor contributing to the surface degradation process is commonly called "hot corrosion" or "sulfidation". Space does not allow a complete treatment of this important subject, but a report on research in progress will allow a qualitative description of what occurs during this process. It is now generally accepted that hot corrosion, in the present context, is caused primarily by the deposition of Na_2SO_4 (this compound is simply a model and other sulfates admixed with the Na_2SO_4 can be part of the model) on the surfaces of turbine hardware.[ ] The compound Na_2SO_4 is formed principally from sodium compounds in the air ingested by the engine and sulfur derived principally from combustion products of sulfur-containing fuel. The hot corrosion process, which results from the interaction of this molten Na_2SO_4 on the alloy surface takes place by the following sequence of events:[ ]

(a) In accord with the thermodynamics of the Na_2SO_4-O_2-alloy system, the first product which forms is the requisite selective oxide.
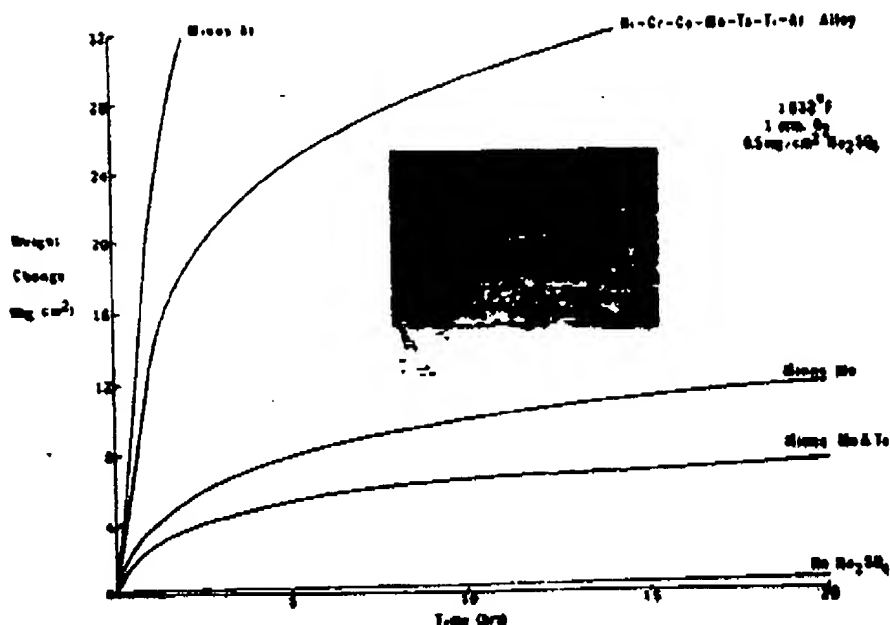
Fig. 7—Effect of various alloying elements on the rate of Na₂SO₄ attack of a nickel-base superalloy. Inset (200X reduced to 50% of original size) illustrates excessive thickness and complexity of the oxide scale formed.

(b) Removal of oxygen from the molten medium by metal oxide formation produces a sulfur/oxygen ratio of sufficient magnitude to cause formaton of metal sulfides (usually chromium sulfide), contiguous with or below the initially formed oxide.

(c) Removal of sulfur from the molten Na₂SO₄ medium increases the concentration of oxide (O⁻) ions in the molten layer, making the medium an excellent solvent for the normally protective oxide; for example

$$Al_2O_{3\,solid} + O^= \rightarrow 2AlO_2^-_{in\ solution}$$

(d) Since no protective oxide is formed under these conditions, a linear (accelerated) oxidation process ensues.

(e) When only a limited supply of Na₂SO₄ is available, the molten medium at some point saturates with respect to the oxide, a protective layer of the oxide re-forms and the accelerated process terminates.

Oxide ions (O⁻) are the basic component in the Na₂SO₄ molten salt system whereas SO₃ is the acidic component. At sufficiently high SO₃ pressures it is conceivable that the molten salt can be sufficiently acidic to also dissolve normally protective oxides. While this mechanism may not be important in the present context, a related process, the continual production of acidic oxides such as MoO₃ from molybdenum in the alloy itself may prevent the hot corrosion process from terminating. That is, hot corrosion, initiated by a relatively small single dose of Na₂SO₄ may proceed to almost total destruction of a fairly massive piece of the alloy.

The accelerating effect of molybdenum is clearly shown in Fig. 7, which illustrates the behavior of a practical alloy coated with a thin layer of Na₂SO₄ and heated to elevated temperature. The complexity and excessive thickness of the non-protective reaction

A tentative explanation of the well known effect of chromium in inhibiting the hot corrosion process appears to lie in the ability of the oxides of this element to act in a "buffering" capacity. That is, on the basic side Cr₂O₃ may consume oxide ions to form chromate (CrO₄⁻) while on the acid side, chromate may contribute oxide ions to neutralize more acidic species. In both cases, a neutral medium, more conducive to protective oxide formation would result. Attempts to rigorously prove this relatively sound hypothesis are the subject of current research.

The data presented in Fig. 7 also tend to indicate that aluminum acts in a beneficial manner although there is some controversy on this point. Also, while titanium has been identified as a beneficial element in some work, the confirmation of its effect in terms of the above described mechanism awaits further research.

It has recently been reported that the addition of fractional percentages of the rare earth element cerium to nickel-base superalloys also markedly inhibits the hot corrosion process. Exactly how this inhibition fits in the proposed mechanism for hot corrosion attack is not yet clear, and is also the subject of current research.

It is important to note that the term "sulfidation" is something of a misnomer with respect to description of the total hot corrosion process. Detailed experiments have shown that the mere presence of sulfides in superalloys which contain aluminum does not cause the catastrophic attack observed with Na₂SO₄. The major role played by sulfide formation in these alloys appears to be the resultant increase of oxide ion concentration in the Na₂SO₄.

COATINGS

It is now common practice to apply some type of protective coating to extend the surface stability of the class of materials under discussion. The importance of aluminum in promoting oxidation resistance of these materials has been clearly defined. It has also

been pointed out that oxidative degradation involves loss of aluminum, as spalled Al_2O_3, from the alloy surface. Thus to extend surface stability or oxidation resistance, the alloy is simply provided with a larger reservoir of aluminum. For all contemporary coatings this is achieved by reacting the alloy surface with a source of aluminum to convert an appropriate thickness of the alloy (usually 1-4 mils) from the normal $\gamma + \gamma'$ structure and composition to an appropriate structure and composition of higher aluminum content. The nickel-aluminum intermetallic phase which has proved to be most suitable as a protective coating is $\beta(NiAl)$, which has a rather wide range of stoichiometry.

Extensive studies on the structures and formation mechanisms of these coatings," coupled with recently published basic diffusion mechanisms in the nickel-aluminum system" now allow a quite detailed description of the properties of this class of protective coatings.

For example, it is now known that only two basic types of these coatings can exist on nickel-base alloys (these are shown in Fig. 8). These types are now described as, first, the inward diffusion type, because this type is formed primarily by singular inward diffusion of aluminum into the substrate alloy, and second, the outward diffusion type, because this type is formed by singular outward diffusion of nickel from the substrate alloy. As these mechanisms of formation are briefly described, it should be recalled that basic diffusion studies by Janssen and Rieck" have shown that in the intermetallic compound Ni_2Al_3 only aluminum can move, and this at a relatively high rate, whereas in NiAl, only nickel can move and this at a relatively low rate.

The initial result of the first process, inward aluminum diffusion, is illustrated in Fig. 9, which shows a predominantly Ni_2Al_3 coating formed by singular inward diffusion of aluminum. This behavior is achieved by regulating the aluminum activity of the appropriate pack cementation process so that the surface phase initially formed is Ni_2Al_3; this is accomplished at essentially unit activity of aluminum. Microprobe analysis confirms that only inward diffusion of aluminum has occurred; all alloying elements and microstructural features of the substrate alloy are present in the coating. Since Ni_2Al_3 is too brittle and too low-melting for practical use as a coating, the system is subjected to further heat treatment, usually in the vicinity of 2000°F, to convert the coating to NiAl. This heat treatment yields the coating structure shown in Fig. 8a.

The following sequence of events occurs during the conversion of the initial Ni_2Al_3 coating to NiAl:

(a) continued diffusion of Al in the Ni_2Al_3 to meet and react with Ni from the substrate to form a layer of single phase NiAl—the so-called denuded zone illustrated in Fig. 8a; and

(b) continuation of this process until Al can no longer diffuse inward; the coating zone; at this

point the process of conversion of the outer zone then proceeds by singular nickel motion from the substrate.

Removal of nickel from the substrate during these processes enriches the substrate in aluminum to a

A

B

Fig. 8—Microstructure of two basic types of diffusion aluminide coatings on nickel-base alloys: (a) inward diffusion type, (b) outward diffusion type (change in color of outer layer due to change in stoichiometry of NiAl) (1000X).
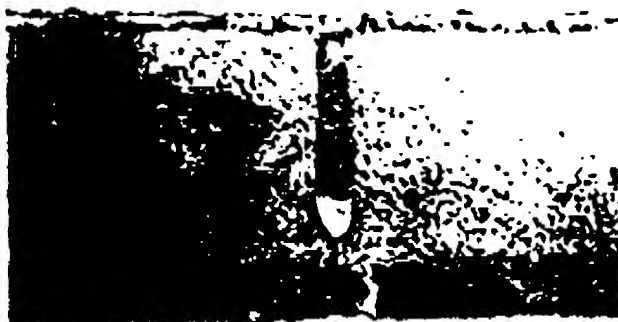
Fig. 9—Microstructure of as-formed coating prepared by singular inward diffusion of aluminum. The larger included particles are MC carbides initially present in the nickel-base alloy (1000X reduced to 90% of original size).

concentration where a phase transformation from $(\gamma + \gamma')$ to $\beta(NiAl)$ occurs, and another layer of this phase (so-called interdiffusion zone) forms and grows, also by nickel motion. Insolubility of most elements in NiAl causes precipitation of a variety of phases (carbides, sigma, etc.) in this zone during its growth.

To prepare the outward diffusion type of coating, shown in Fig. 8b, the aluminum activity of the pack cementation coating medium is adjusted so as to cause NiAl to be the phase initially formed. This is achieved by alloying the aluminum with suitable amounts of other elements such as chromium, cobalt and nickel. The coating then grows by outward diffusion of nickel from the substrate, through the growing NiAl layer to react with aluminum at the external surface. The interdiffusion zone is formed as before, by nickel removal from the substrate. It is to be emphasized that there are no other types of

NiAl coatings within the range of our experience and practicality. Coatings made by two steps, e.g., pre-chromizing and then aluminizing also fall into this system of classification. Although detailed studies on the mechanisms of formation of CoAl coatings on cobalt-base alloys are not complete, research in progress indicates that in a general way the same types of mechanisms occur.

These coatings degrade according to the two general mechanisms previously described—oxidation accompanied by Al_2O_3 spalling, and hot corrosion. Surface stability is extended beyond that of the substrate alloys because of the larger amount of aluminum available. Minor differences in performance, usually caused by substrate elements and secondary substrate phases included in the coatings can be observed, but in general all of these coatings exhibit about the same lifetime for a given thickness and aluminum content of the coating.

It has been widely speculated in the past that loss of aluminum by diffusion into the substrate alloy constitutes a major degradation mode of this type of coating. This is a rather inaccurate generalization that does not always hold up when practical boundary conditions for use of the coatings are applied. Up to the practical upper temperature limits imposed by the strengths of the substrate alloys it has been found that under realistic dynamic-cyclic oxidation conditions, by far the greatest loss of aluminum is by the oxide spalling process (or hot corrosion) with only a relatively small amount being lost to the substrate during the useful oxidation lifetime of the coatings.[n,o] This situation occurs because of the low diffusion rates in the $\beta(NiAl)$, γ and γ' phases and also because of the parabolic rate laws governing the diffusion processes. Therefore, until the oxide spalling loss is significantly decreased, the search for so-called "diffusion barriers" does not make a great deal of sense.

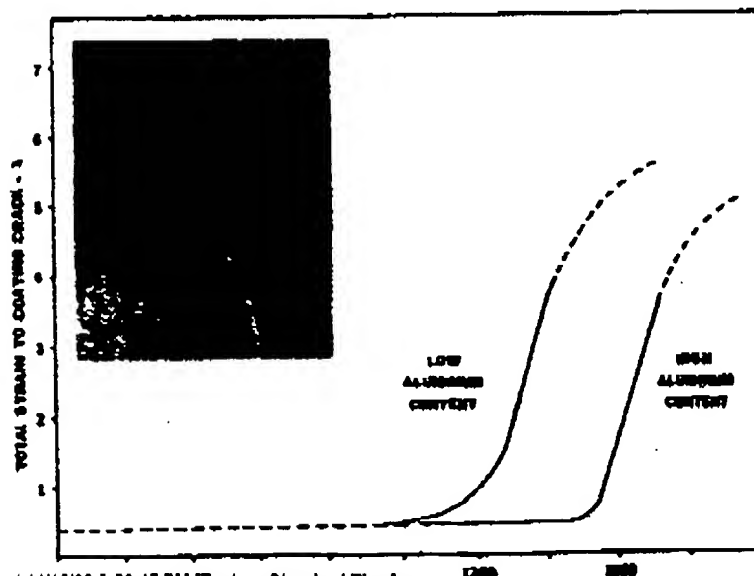The effects of these coatings on the mechanical behavior of the coating-alloy composite system are

Fig. 10—Schematic illustration of brittle-ductile transition behavior of aluminide coatings. Inset (750X reduced to 50% of original size) shows the result of straining a coating beyond the fracture limit.

Fig. 11—Schematic comparison of dynamic-cyclic oxidation behavior of diffusion aluminide coating and advanced overlay coating on a nickel-base alloy (inserts 500X reduced to 50% of original size).
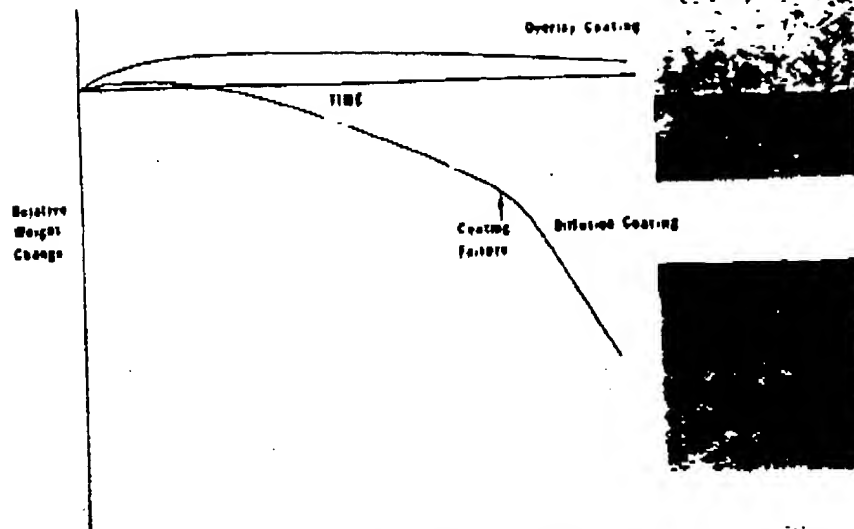
rather subtle." With some qualifications, provided that the heating cycles used for formation of the coatings and subsequent diffusion heating cycles are compatible with strengthening heat treatments applied to the base alloy, creep behavior is unaffected. The qualifications include due consideration of the ratio of coating to alloy cross section; for thin alloy sections, e.g., 20 mils of alloy, 3 mils of coating per side, appropriate corrections must be made to account for the fact that the coating is essentially non-load bearing.

The effects of diffusion coatings on thermally or mechanically induced fatigue cracking are somewhat more profound. For example, as expected NiAl coatings exhibit a brittle-to-ductile transition behavior as shown in Fig. 10. Also, as expected, the transition temperature is dependent on the aluminum content of the NiAl, decreasing with decreasing aluminum content within a limited range. The result of straining a coating beyond its ductility limit is also shown in Fig. 10. Procedures for design of turbine blades and vanes must take account of these coating properties.

Obtaining improvements in the performance of this class of coatings, while at the same time maintaining reasonable cost effectiveness is a difficult proposition. From the previous discussion of improvements to be gained by enhancement of oxide adherence it is reasonable to assume that similar improvements could be achieved in coatings. Unfortunately, it can also be concluded from the discussion of formation mechanisms of diffusion coatings that the incorporation of reactive metals to produce enhanced oxide adherence is difficult if not practically impossible. On the other hand, improvements in hot corrosion resistance can be effected by incorporation of additional chromium in external layers of the coating," but some decrease in oxidation resistance might be expected because this chromium must be present as a secondary phase, insoluble in NiAl.

design and synthesis of ideal coating compositions— idealized or maximized in terms of oxidation and hot corrosion resistance—applied to the alloy surface in a manner such that the coating composition is more or less independent of, but still compatible with the alloy." Fig. 11 schematically illustrates the comparative behavior of this overlay type of coating and a contemporary diffusion coating. The advantage of enhanced oxide adherence is shown and it should also be inherently evident that other desirable elements, for resistance to hot corrosion, for example, can be incorporated in these coatings in a controlled manner The mechanical properties of these coatings can also be optimized along with oxidation and hot corrosion resistance. As higher temperatures are encountered in advanced engines this advanced type of coating will displace the contemporary diffusion coatings to the lower temperature stages of the turbine.

REFERENCES

[1] Pettit, F. S.: Transactions AIME, Vol. 239, 1967, p. 1296.
[2] Giggins, C. S. and Pettit, F. S.; Transactions AIME, Vol. 245, 1969, p. 2495.
[3] Wukusick, C. S. and Collins, J. F.; Materials Research and Standards, Vol. 4, 1964, p. 637.
[4] Sims, C. T., Bergman, P. A. and Beltran, A. M.: "Program in the Development of Hot-Corrosion-Resistant Alloys for Marine Applications". Gas Turbine Division, ASME Gas Turbine Conference and Products Show, Cleveland, Ohio, March 9-13, 1969.
[5] Piearcey, B. J. and VerSnyder, F. L.: Metal Progress, Vol. 90, 1966, p. 66.
[6] Boyd, J. A. and Pettit, F. S.: Metallurgical Transactions, accepted for publication.
[7] Goebel, J. A. and Pettit, F. S.: Metallurgical Transactions, accepted for publication.
[8] Bornstein, N. S. and DeCrescente, M. S.; Transactions AIME, Vol. 245, 1969, p. 1947.
[9] Goward, G. W., Boone, D. H. and Giggins, C. S.; Transactions Quarterly, Vol. 60, 1967, p. 228.
[10] Janssen, M. M. P. and Rieck, G. D.: Transactions AIME, Vol. 239, 1967, p. 1372.
[11] Redden, T. K.; Transactions AIME, Vol. 242, 1968, p. 1695.
[12] Boone, D. H. and Goward, G. W.: "The Use of Nickel-Aluminum Intermetallic Systems as Coatings for High Temperature Nickel-Base Alloys", Proceedings of the Third Bolton Landing Conference, Claitor's Publishing Division, Baton Rouge, 1970, p. 545.
[13] Bartocci, R. A.: "Behavior of High-Temperature Coatings for Gas Turbine Engines", ASTM STP 421, 1967, p. 169.
[14] Bradley, E. F., Rainey, D. O. and Donachie, M. J., Jr.: Metal Progress, Vol. 97, 1970, p. 60.

hot corrosion, and ... have led to the